COMBUSTION

DEVOTED TO THE ADVANCEMENT OF STEAM PLANT DESIGN AND OPERATION

6, No. 11 | MAY, 1935 | 25c a copy

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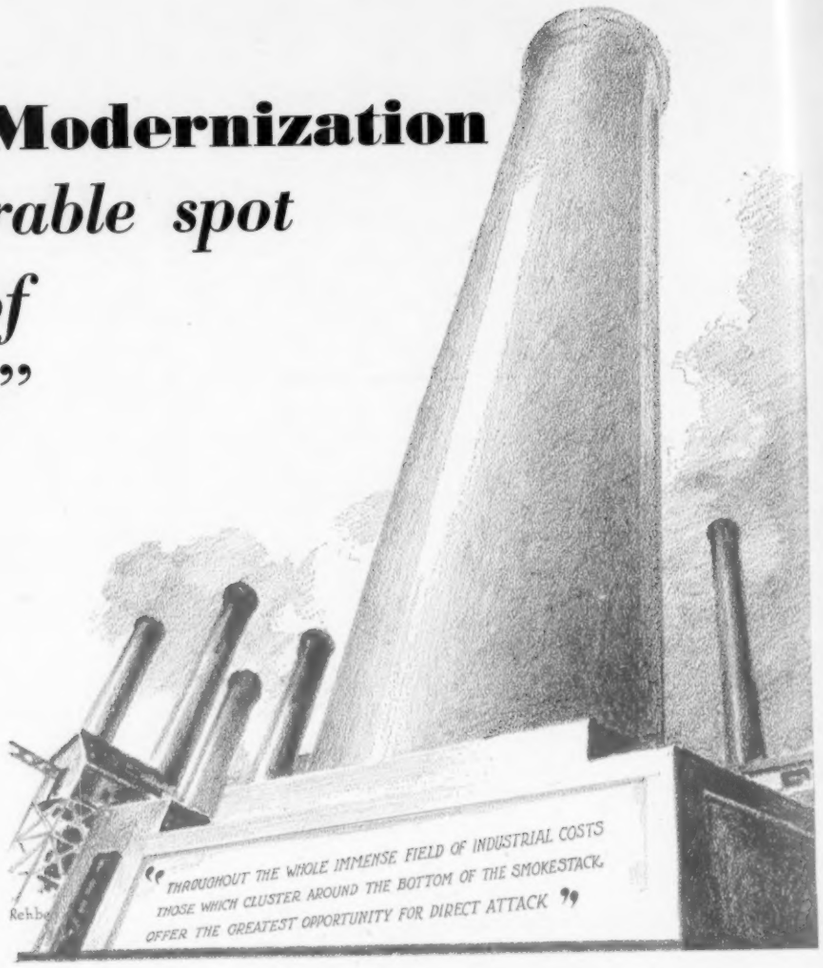
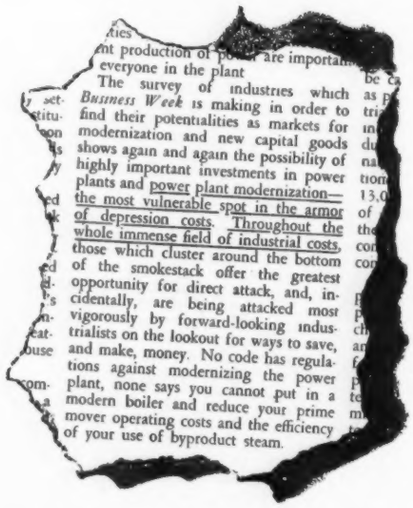
One of the new 330,000 lb per hr 710 lb pressure boiler units in the Connors Creek Station, Detroit

Centrifugal Boiler Feed Pumps for High Pressures

Dissociation of Products of Combustion

"Power Plant Modernization *the most vulnerable spot in the armor of depression costs"*


"THROUGHOUT THE WHOLE IMMENSE FIELD OF INDUSTRIAL COSTS THOSE WHICH CLUSTER AROUND THE BOTTOM OF THE SMOKESTACK OFFER THE GREATEST OPPORTUNITY FOR DIRECT ATTACK"



...ties ...nt production of power are important to everyone in the plant

The survey of industries which *Business Week* is making in order to find their potentialities as markets for modernization and new capital goods shows again and again the possibility of highly important investments in power plants and power plant modernization—the most vulnerable spot in the armor of depression costs. Throughout the whole immense field of industrial costs, those which cluster around the bottom of the smokestack offer the greatest opportunity for direct attack, and, incidentally, are being attacked most vigorously by forward-looking industrialists on the lookout for ways to save, and make, money. No code has regulations against modernizing the power plant, none says you cannot put in a modern boiler and reduce your prime mover operating costs and the efficiency of your use of byproduct steam.

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COMBUSTION

DEVOTED TO THE ADVANCEMENT OF STEAM PLANT DESIGN AND OPERATION

VOLUME SIX NUMBER ELEVEN

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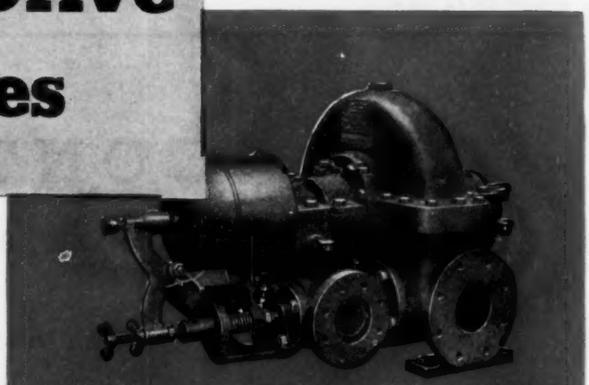

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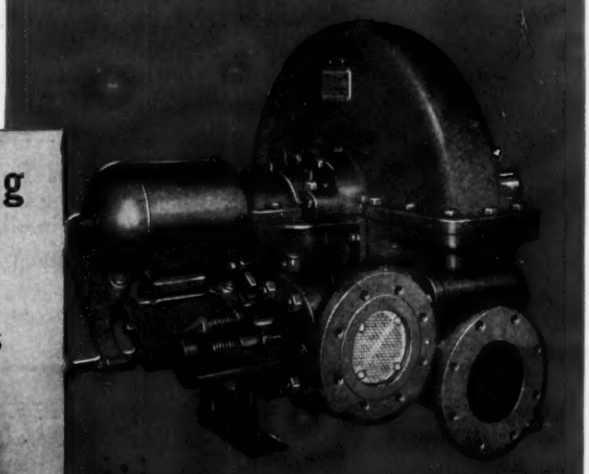

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EDITORIAL

Pending Coal Legislation

The Senate Committee on Interstate Commerce has reported favorably on the pending Guffey bill, the stated purpose of which is "stabilization of the bituminous coal industry." Regarding coal as a public utility, the bill provides for the setting up of a National Bituminous Coal Commission whose functions would go beyond mere governmental regulation, as ordinarily understood. Certain sections of the bill are analogous to those already applied to agriculture, in that restriction of output is provided. To this end opening of new mines or mines not operated since 1929 is forbidden, except by permission of the Commission, and an initial federal expenditure of three hundred million dollars is proposed for the purchase of coal mines and properties to be withdrawn.

Coal prices are to be fixed by District Boards functioning under the control of the National Commission. Producers are coerced into joining the code by the imposition of a drastic tax, 99 per cent of which is refunded to those who do join.

Over a period of years many attempts have been made to bring about some degree of stabilization within the bituminous coal industry, through agreement among producers. It will be recalled that this formed one of the major objectives of the Third International Coal Conference, held in Pittsburgh in the fall of 1931. However, the large number of independent coal properties and the competitive situation made this difficult.

Enactment of the Guffey bill would undoubtedly benefit some producers, despite the encumbrance of federal supervision, whereas other producers are strenuously opposing such legislation. From the standpoint of the consumer, however, it would be certain to result in higher coal prices. This, in turn, would have bearing on future steam plant designs.

New Engineering Corporations Prohibited in New York State

"No corporation formed after April 15, 1935, shall practice or offer to practice professional engineering in New York State, and no corporation hereafter formed may use or assume a name involving the word 'engineers' or 'engineering' or any modification of such terms except a non-profit membership corporation composed exclusively of professional engineers. Engineering corporations which were previously organized and practicing engineering may continue to do so, provided the chief executive officer of the corporation and all employees carrying on the actual practice of engineering for the corporation are licensed professional engineers. All corporation employees who are designated as 'engineers' are also required to be licensed professional engineers. Furthermore, no existing engineering corporation is permitted to change its name, or transfer its corporate rights without consent of the State Education Department."

Such is the substance of an amendment to the New York State Engineers' Licensing Law, which became effective last month. This amendment, which was sponsored by the State Board of Engineering Examiners and by the New York State Society of Professional Engineers was aimed at numerous companies and contracting firms which have appropriated the terms "engineers" or "engineering," and solicited business on this basis, without possessing the necessary qualifications as to its personnel. Furthermore, it was intended to correct a loop-hole in the original law which permitted those who were denied a professional license, or who were under charges of practicing engineering without license, to incorporate and defy the intent of the law.

From this it would appear that engineering firms formed *in the future* must be in the name of an individual or a partnership—a practice that obtains in the legal profession. It may be argued with justification that a corporation, made up of experienced engineers and specialists is better qualified to carry out engineering work of large magnitude than an individual consultant whose experience is necessarily limited, and that the necessary protection is afforded by the requirement that its engineers be licensed. Undoubtedly, many ways will be found to comply with the terms of the law legitimately without incurring unnecessary burdens.

A Notable Address

Those who were privileged to listen to the address of President Flanders of the A.S.M.E. before the Metropolitan Section on May first pronounced it one of the clearest analyses of the present economic situation that has yet been offered. Mr. Flanders reviewed the various efforts of the Government, commended some, constructively criticized others, and took issue with the assertion that our highly developed mechanization of industry has contributed largely to unemployment and present ills. In his opinion, the effort to increase both wages and prices is retarding recovery by failing to increase purchasing power, by restricting foreign trade and by hindering new privately financed construction. If wages were held stationary and prices lowered, purchasing power and construction would be stimulated. Distinguishing between the evils of speculative profits and the benefits of legitimate industrial profits, Mr. Flanders urged that such reforms as have already been enacted are adequate to cover the former and that further reforms at this time will retard business.

Although delivered by an engineer before a large group of engineers, President Flanders' remarks would have intensely interested business men in all lines. However, despite its excellence and broad appeal, one searched the metropolitan dailies in vain the next day without finding any mention of the address. This is just another instance of the failure of the engineering profession to get its ideas before the general public.

Centrifugal Boiler Feed Pumps for High Pressures

By **A. PETERSON** Chief Engineer
Pump and Compressor Dept.
DeLaval Steam Turbine Co.,
Trenton, N. J.

Employment of high steam pressures introduced new problems in boiler feed pump design, involving casing, diaphragms, balancing and stuffing boxes, etc., in order to prevent leakage, both external and internal; also the higher water temperatures necessitated a greater differential between pressure on the suction and the vapor pressure corresponding to the temperature. These factors are discussed, as well as operating problems and constant versus variable-speed drive. American and European practices are compared.

WHEN the centrifugal pump was first used for boiler feeding, the steam pressures and water temperatures were so low that standard multistage pumps gave satisfactory results. The steam pressures did not often exceed 200-lb gage, nor the water pressures 250 lb, which with a maximum water temperature of around 212 F made the problem of designing a pump comparatively easy.

About the only thing that the designer had to look out for was that sufficient pressure on the suction above the vapor pressure corresponding to the temperature of the water was available. The factors which affect cavitation were not at that time very well known and it sometimes happened that a boiler feed pump to handle 212 F water was installed with only 6 to 8-ft head on the suction and without proper regard to the speed of the pump. The result was lack of capacity, cavitation and noise, with consequent corrosion of the first stage impeller. By experience it was found that a head of 12 ft on the suction for 212 F water resulted, as a rule, in satisfactory operation, provided excessive speeds were not used. Present practice is to specify such a pressure for both low-pressure and high-pressure boiler feed pumps.

Effect of Higher Water Temperatures

For the higher water temperatures encountered in high-pressure plants, it is recommended that a greater differential between pressure on the suction and the vapor pressure corresponding to the water temperature be used. This is explainable by the fact that a 12-ft differential at a water temperature of 400 F results in a flashing margin of only about 1.6 deg, whereas this margin with 212 F water is 15 deg. Recent experience with boiler feed pumps for high temperatures has shown that it is not necessary to provide as great a temperature differential for high water temperatures as for low temperatures. For 400 F water temperature, a head on the suction 25 to 30 ft higher than that corresponding to the temperature is generally sufficient, which provides a temperature differential of from 3.3 to 4 deg.

The introduction of high steam pressures and temperatures gave the designer many exacting requirements to meet and several years of costly development and experimental work were required to produce a pump satisfactory for boiler feed service. The combination of high pressure and high temperature made it difficult to build a tight pump casing, as the high temperature introduced expansion and alignment problems that were not easy to solve. With very hot water, with consequent high suction pressures, the matter of shaft packing became extremely perplexing. In fact, much still remains to be done to reach the goal of an entirely satisfactory stuffing box for a water temperature of, say, 450 F and a pressure on the suction of around 500 lb with a large diameter shaft running at 3500 rpm. While this would seem to be a problem for the packing manufacturers, the pump manufacturers, and also the operators, have been forced to do considerable experimental work to keep the pumps in operation without frequent shutdowns for repacking.

Design of Pump Casing for High Pressure

In the United States the pump with horizontally split casing has predominated, as contrasted with the drum and ring casing in Europe. Its outstanding advantage is, of course, the ease with which it can be disassembled for inspection or repairs.

For pressures up to 600 lb and even 800 lb, no difficulties were experienced in obtaining tight pump casings, but when pressures were suddenly jumped up to around 1600 lb, it was not easy to make the horizontally split pump tight, and this is true not only as to external tightness, but also as to internal tightness to prevent leakage between stages and around diaphragms and rings. The internal leakage is the more serious because it cannot be seen and often results in cutting out of the casing.

The horizontally split multistage pump shown in Fig. 1 is suitable for a pressure of about 1600 lb, and a water temperature of approximately 275 F. As can be seen in Fig. 2, the pump casing is supported close to the plane of the axis of the shaft in order to eliminate misalignment of the coupling caused by changes in temperature of the water. The pump casing has extremely heavy flanges and bolting.

The partitions between stages are not cast integral with and, therefore, split with, the casing, but are solid diaphragms. With integral partitions, there is always a certain possibility that leakage will occur between the stages, which often are subjected to a pressure difference of 200 lb or more, and no matter how slight the leak, cutting out of the pump casing then ultimately results. The long bolts through these partitions will stretch, and that leakage is expected is evident from the special cap nuts often used for such bolts, which keep the leakage from becoming visible. The solid diaphragms between the stages in the pump shown in Fig. 1 are of large diameter, so that the tongue and groove joint is close to the flange bolts and the radial extension of the casing partition toward the shaft is, therefore, short and easily held tight by the heavy flange bolts.

The pump has a solid end cover, the main purpose of which is to clamp the stationary balancing ring tightly against the casing. The pressure drop across the balancing ring is approximately equal to the pressure generated by the pump and the ordinary tongue and groove joint as used on low pressure pumps is not sufficient to tighten against a pressure as high as 1600 lb. The casing of high pressure boiler feed pumps is almost invariably made from cast steel.

The drum type of pump casing, as used by European pump builders, and to a small extent in this country, is shown in Fig. 3. The ring type, also a European product, is shown in Fig. 4. As may be seen, disassembling and assembling is an extremely tedious job. If new parts are installed, it is difficult to check clearances, etc., and if trouble is experienced in starting, the pump may have to be again completely disassembled.

Balancing Arrangement

The balancing device preferred for high-pressure pumps is the disk with a radial leak-off, as it can be made to operate satisfactorily with less leakage than can the balancing drum, as shown in Fig. 5. The axial bleed-off bushing which controls the leakage is subject to a comparatively small drop in pressure and, therefore, is not subject to much wear. The balancing drum, on the other hand, is subject to a drop in pressure equal to the pressure generated by the pump and wear, therefore, becomes quite serious. Practically all European pumps employ the disk balancing arrangement.

High-pressure pumps are sometimes built with single-suction impellers arranged back to back, but such pumps are not completely hydraulically balanced. Furthermore, one of the stuffing boxes is subjected to a pressure considerably higher than the suction pressure, and some of the interstage bushings within the pump are also subjected to great pressure differences.

Stuffing Box Design

By proper selection of sleeve material and packing, it is now possible to operate at higher rubbing speeds, higher pressures and higher temperatures than were dreamed of a few years ago. One quite outstanding record is a 1600-lb pump that was in operation for over 9000 hrs without being repacked, pumping water at 210

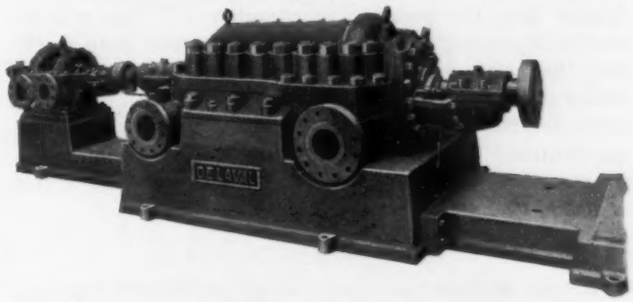


Fig. 2—Photograph of split casing pump, showing support near the plane of the axis of the shaft

F temperature and 325 lb suction pressure. The speed of the pump is 3500 rpm and the sleeve diameter $3^1/_4$ in. No bleed-off was used. However, had the temperature of the water corresponded to the pressure on the suction, which would have meant a water temperature of about 425 F, the packing problem would have been more difficult. Arrangements to cool the packing would become necessary and several schemes have been tried to accomplish this. Cooling chambers around the outside of the stuffing box are used, but such means are not effective; about all that is accomplished is that the stuffing box feels cool to the hand. Far more effective is cooling the inside of the shaft sleeve, which can be done through a hole in the shaft, as shown in Fig. 6, or as shown in Fig. 7, the latter being a European design.

A still more effective method of cooling the stuffing box is shown in Fig. 8. If water at a temperature of, say, 500 F were being pumped, the suction pressure would need to be around 725 lb. This pressure is bled down through the labyrinth rings to chamber *C* to a pressure of about 300 lb. Into chamber *E* cold water,

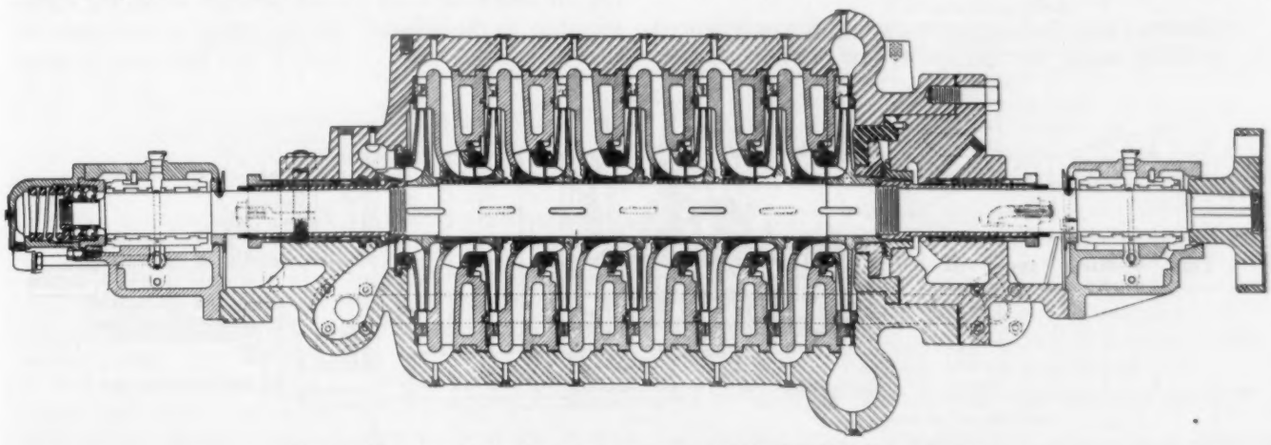


Fig. 1—Section of a split casing pump suitable for 1600 lb pressure

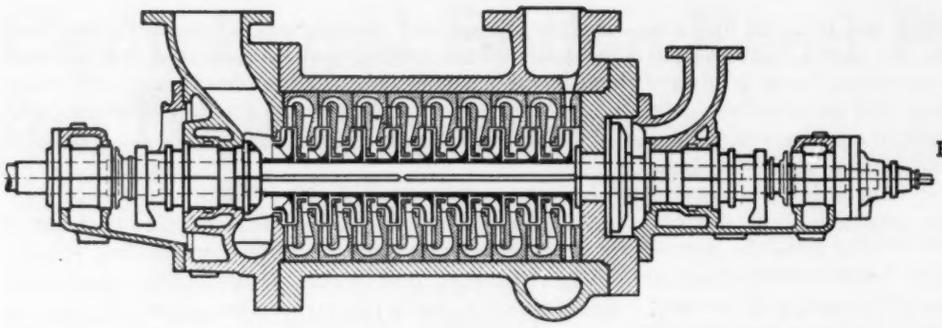


Fig. 3—Drum type of pump casing

or water of a temperature as high as the packing can safely withstand, is introduced at a pressure slightly higher than the pressure in chamber *C*. This will effectively prevent the high temperature water from reaching the soft packing. Fig. 9 shows temperatures of water corresponding to different pressures and, therefore, indicates the severe operating conditions which may be encountered in pumping water at high temperatures. In regard to packing materials, it has been found that a metallic packing on a hard steel sleeve is best.

Rotor Design

Bronze has always been considered the best material for pump impellers, but because of the considerable difference in expansion between bronze and steel, other materials, such as steel or monel metal, are used in high temperature pumps.

In order to avoid too great a number of stages, high-pressure boiler feed pumps are, as a rule, designed with high pressures per stage, up to around 200 lb in stationary power plant practice and as high as 500 lb in naval practice. This, naturally, puts a premium on means for minimizing the leakage from the discharge to the suction chambers of the impeller. Small clearances have been used at these points, but an initially small clearance between the rings will increase rapidly from wear, with consequent loss in efficiency. By equipping the pump with labyrinth wearing rings, two and one-half to three times greater clearance can be used without more leakage than would occur through a set of flat wearing rings. The considerably lower water velocity through the labyrinth rings naturally results in less wear and, therefore, in far better sustained efficiency, which is of great importance in reducing the high power consumption of high-pressure boiler feed pumps.

Operation of High-Pressure Boiler Feed Pumps

Difficulties with flashing have always been experienced in operating boiler feed pumps at low delivery or near shut-off, particularly when the pressure on the suction is low for the temperature. This is due to heating of the water in passing through the pump. In high-pressure pumps, the losses at low delivery are relatively great and the water will be heated more, with consequent greater danger of flashing. Fig. 10, taken from a European publication, shows that the increase in temperature is considerable, and credit for the rise in temperature has even been taken in calculating the pump efficiency, which, however, has not been proposed in this country. It really is not improper to take credit in the heat balance for the additional heat put into the water by the pump although, as compared with the use of bled steam, this is a

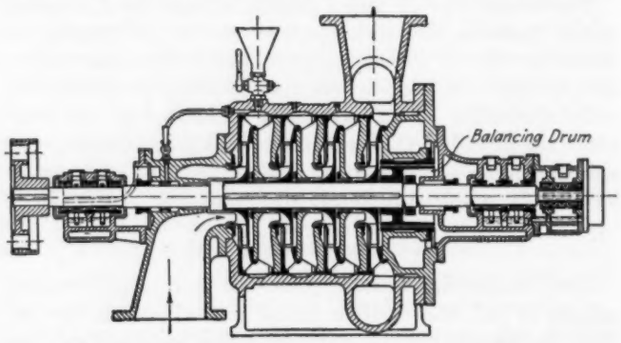


Fig. 5—European drum-balancing arrangement

highly expensive way to heat boiler feedwater. As may be noted from the curve, the temperature rise, even for a delivery somewhat greater than 10 per cent rated capacity, is about 25 F. If the balancing leakage, which is discharged at this higher temperature, be admitted to the suction of the pump, flashing may result, because in pumps handling water at temperatures between 300 and 500 F there is often only from 2 to 5 deg difference between the temperature of boiling corresponding to the pressure and the actual temperature, so that at low deliveries or shut-off, the balancing leakage

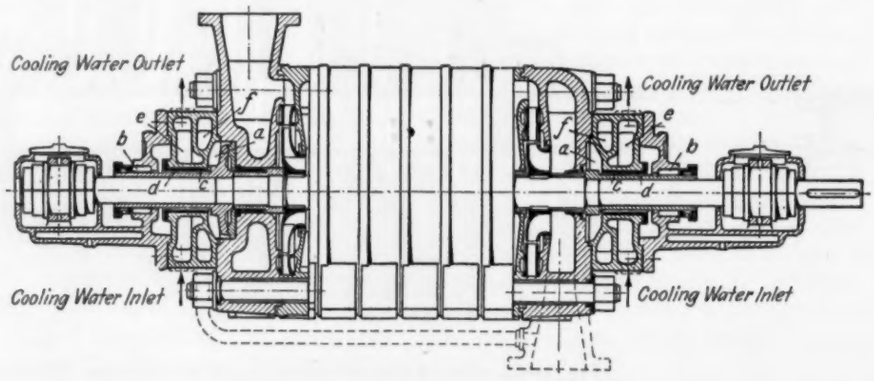


Fig. 4—Ring type of pump casing

may easily cause flashing. This can be avoided by discharging the balancing leakage into the heater. By means of a three-way cock, as shown in Fig. 11, the leakage can be discharged either into the suction or into

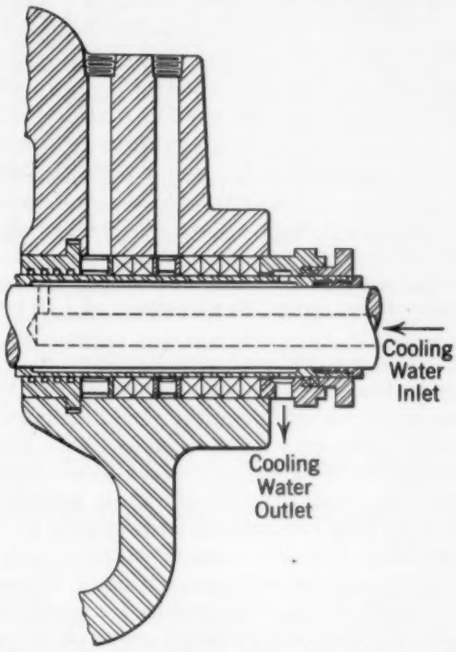


Fig. 6—Method of cooling stuffing box by circulation of water through hollow shaft

the heater, the valve being so designed that the leakage cannot be shut off completely. The efficiency of the pump is not reduced by discharging the leakage into the heater.

In high-pressure plants it has been common practice to install primary and secondary feed pumps, with feedwater heaters between the two pumps, so that the secondary pumps may be handling water at temperatures up to 500 F, with corresponding pressure on the suction. In view of the greater specific volume of hot water, more power is taken to pump a certain weight of hot water against a fixed pressure in pounds than to pump cold water. Naturally, feedwater heaters designed to withstand full delivery pressure are more expensive than

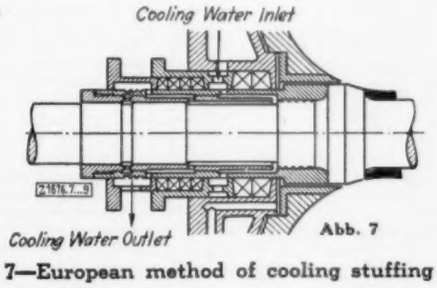


Fig. 7—European method of cooling stuffing box

heaters for lower pressures, but the saving in power may sometimes offset this additional cost and, further, less operating difficulties will be experienced with the cold water pump.

Taking as an example a feed pump for 750,000 lb of water per hour, discharging against 1600 lb pressure, with the secondary pump receiving water of 400 F, with a pressure on the suction of 250-lb gage, such a pump would require approximately 1850 brake horsepower. If the pump were designed for 100 F water, the horsepower required would be approximately 1590, or a saving of 260 hp, which would go a long way toward paying for the additional cost of a heater built to withstand 1600 lb pressure. Fig. 12 shows the specific gravity of water and conversion factors from pounds pressure to feet of water for different temperatures. The saving in power is practically proportional to difference in density of the

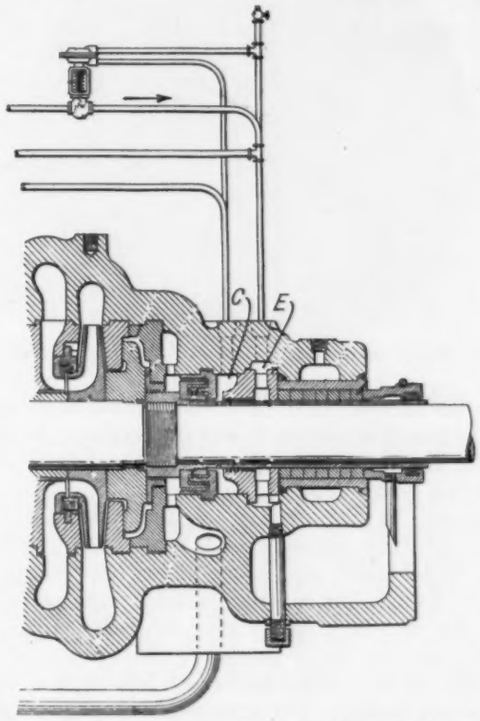


Fig. 8—An American method of cooling stuffing box

water, the relation being expressible either as pumping a greater volume against the same pressure, or the same weight through a greater head.

In the foregoing example, the pump for hot water would be designed for a capacity of nearly 1750 gpm against a net head of 3630 ft, while the capacity of the cold water pump would be only 1500 gpm against a net head of 3120 ft. The pump handling hot water is more expensive on account of the special packing box construction required.

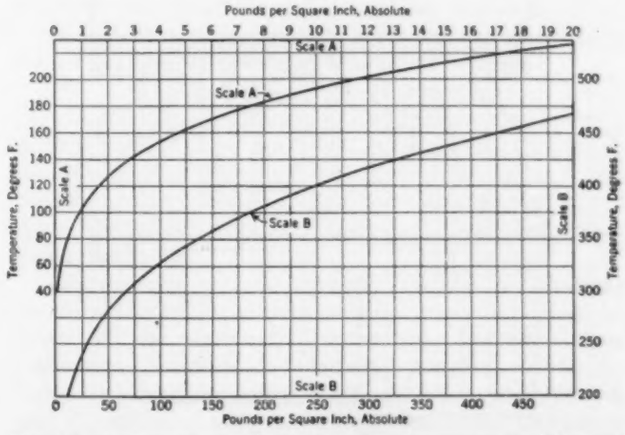


Fig. 9—Temperatures of saturated water vapor at different absolute pressures

Constant Speed versus Variable Speed of Centrifugal Boiler Feed Pumps

In the early days of centrifugal boiler feed pumps, the pump suction drew directly from an open feedwater heater, and, as heaters were seldom used between the pump and boiler, an excess of pump discharge pressure

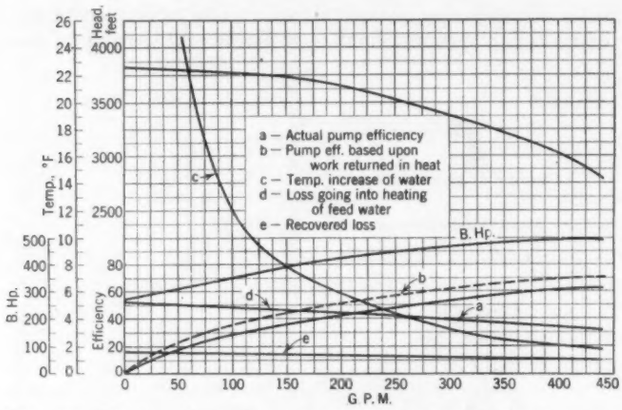

Head, feet
Temp., °F
B. Hp.
Efficiency
a — Actual pump efficiency
b — Pump eff. based upon work returned in heat
c — Temp. increase of water
d — Loss going into heating of feed water
e — Recovered loss
B. Hp.
G. P. M.

Fig. 10—Work returned as heat in the boiler feed pump

over boiler pressure of from 25 to 50 lb per sq in. was sufficient. For this reason, it was unnecessary, or did not as a rule pay, to use variable-speed a-c motors for driving such boiler feed pumps.

However, in the modern high-pressure plant with heaters between primary and secondary pumps and closed feed heaters and economizers between the feed pump and the boiler, the net pressure required from the feed pump at full capacity may be from 200 to 300 lb higher than the boiler pressure. At reduced delivery there will be, of course, materially less friction through heaters and piping. For example, at half capacity the friction head will be approximately one-fourth of what it is at full capacity. This means that a considerable saving in power may be effected by operating the pump at reduced speed. The saving in power results not only from the lower excess pressure, but also from the fact that the head generated by the pump at constant speed

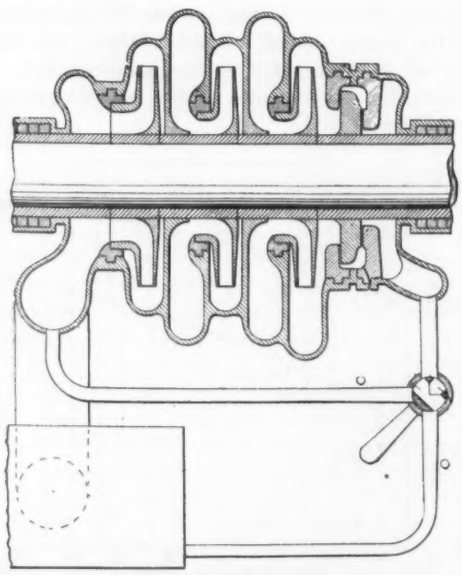


Fig. 11—Arrangement for discharging balancing leakage into heater at low pump delivery

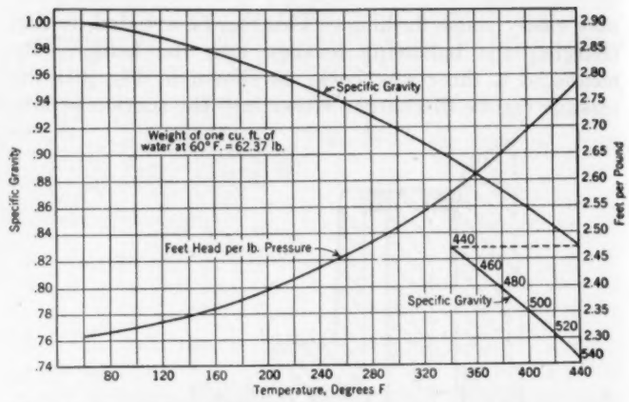

Specific Gravity
Weight of one cu. ft. of water at 60° F. = 62.37 lb.
Feet Head per lb. Pressure
Specific Gravity
Feet per Pound
Temperature, Degrees F

Fig. 12—Specific gravity of water at various temperatures, with heads corresponding to a pressure of 1 lb per sq in.

rises as delivery is reduced, which will produce an appreciably higher excess pressure at reduced delivery than at full capacity. Therefore, at around one-half capacity of the pump, there may be as much as 100 lb, due to the steepness of the head-delivery curve alone, which can be avoided by operating the pump at reduced speed. This, coupled with the reduced friction head to be overcome, may make possible a considerable saving in power. Boiler feed pumps are seldom operated at full capacity, so that it is quite desirable to provide for speed variation.

Fig. 13, showing the pressure required at different deliveries and the corresponding powers taken by a constant speed pump, together with the power and corresponding speeds of a variable-speed pump, is based upon the requirements of a large central power plant. The unit consisted of primary and secondary pumps similar to the unit shown in Fig. 2. In addition to turbine driven pumps for standby service, pumps driven by variable-speed a-c motors were purchased. The additional cost of the variable-speed motor was fully warranted in view of the large saving in power obtained. Although the efficiency of the slip-ring a-c motor drops in approximately the same ratio as the reduction in speed, there is still a large net saving in input to the motor by reason of the fact that the pressure generated by the pump drops as the square of the speed.

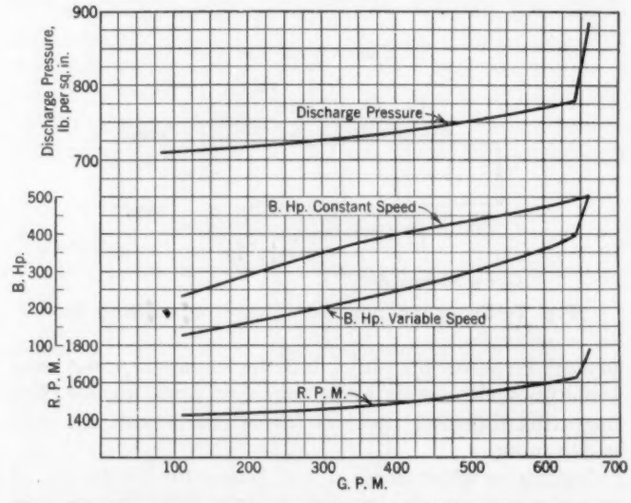


Fig. 13—Excess pressure required at different pump deliveries and corresponding power consumption of constant speed and variable speed pumps

Variable speed for driving boiler feed pumps is obtainable by several means, including:

1. Steam turbine drive.
2. Direct-current variable-speed motors. These are very efficient but not frequently used because of low speed of large direct-current motors.
3. Alternating-current variable-speed motors. When separately driven primary and secondary pumps are used, it is common practice to provide speed variation only for the primary pump.
4. Variable-speed hydraulic coupling. This drive has recently been introduced into this country, but has been used abroad for many years in similar applications. The efficiency is almost as high as obtained with the standard variable-speed a-c motor. The hydraulic coupling has the advantage that speed reduction is gradual and not in steps, and, further, synchronous motors may be used.

An Unusual Boiler Scale

By LEWIS B. MILLER, Johns-Manville Research Laboratories, Manville, N. J.

BOILER scales consisting chiefly of magnesium hydroxide, although not unknown, are somewhat rare. Recently one of this type was encountered. Since information is available both upon the raw water and the boiler treatment used during the time this scale was forming, data are here given upon the raw water, the water treatment and the scale characteristics. It is believed that these data are of real value to those concerned with the problem of boiler water treatment. Partial analyses of the raw water averaged:

	Parts per million
Suspended matter	trace
Dissolved solids	327
SO_3	24
Cl	39
SiO_2	4
R_2O_3	1
CaO	32
MgO	96
Na	trace
Organic matter	trace
Phenolphthalein alkalinity expressed as $CaCO_3$	16
Methyl orange alkalinity expressed as $CaCO_3$	207

The raw water was treated with $^1/_2$ lb of soda ash per 1000 gal of water.

During operation of the boilers (at 75 to 100 per cent of rating) a single sample of boiler water was taken from the bottom water gage. Partial analysis of the boiler water is as follows:

Total solids	4200 ppm
Dissolved solids	2400 ppm
Suspended solids	1800 ppm
Phenolphthalein titration expressed as $CaCO_3$	13 ppm
Methyl orange titration expressed as $CaCO_3$	66 ppm
SO_3 in solution	257 ppm

Analysis of the scale removed from the tubes is as follows:

Loss on drying at 100 C	0.61 per cent
Loss on ignition	29.3 per cent
CO_2	1.1 per cent
SiO_2	1.2 per cent
Fe_2O_3	1.0 per cent
Al_2O_3	0.3 per cent
Mn_3O_4	0.3 per cent
CaO	4.3 per cent
MgO	57.8 per cent
SO_3	5.0 per cent

Calculation indicates that approximately 85 per cent of the scale is probably magnesium hydroxide, $Mg(OH)_2$, and 9 per cent is anhydrite, $CaSO_4$.

Petrographical microscopic analysis of the $^3/_{16}$ in. thick scale showed a somewhat fibrous structure, the fibers occurring radially with respect to the boiler tubes.

Photomicrograph of scale immersed in oil

Because of the fineness of the structure it was very difficult to determine the nature of the scale by optical methods alone. The results of the petrographical study indicated, however, that the scale probably consisted of amorphous or microcrystalline magnesium hydroxide cemented together by interspersed anhydrite needle crystals, $CaSO_4$. The illustration is a photomicrograph of fragments of the scale immersed in an oil. The fibrous nature is apparent in the larger fragments.

Exhibit to Feature A.S.T.M. Meeting

During the five days of the Thirty-eighth Annual Meeting of the American Society for Testing Materials at Detroit, June 24 to 28, there will be an exhibit of testing apparatus and related equipment. This will include, in addition to displays by leading companies in the testing instrument and related apparatus field, an exhibit of non-commercial apparatus sponsored by A.S.T.M. committees or research laboratories for the carrying out of special tests and research work. In this group of displays there will be a special high-speed fatigue-testing machine, a low-capacity impact machine, a machine for making bending tests and apparatus used for special tests of insulating materials.

The A.S.T.M. Committee on Corrosion of Non-Ferrous Metals and Alloys plans to have an extensive display of the large number of atmospheric, galvanic, electrolytic and immersed test specimens which it has collected, and the Committee on Metallography will sponsor a special display of photographs and other material in this field.

The meeting will be formally opened on Tuesday morning (June 25) with an address by C. F. Hirshfeld, Chief of the Research Department, Detroit Edison Company. Sessions on Thursday morning will be devoted to corrosion and to coal and coke, while fatigue and the effect of temperature on metals will be considered on Thursday evening.

Heating Values of Fuels

By J. S. DOOLITTLE
Ass't. Prof. of Mechanical Engineering
The Pennsylvania State College

THE heating value of a fuel, as commonly understood is "the heat removed when a unit amount of the fuel is completely burned and the products of combustion are cooled down to the temperature of the original air-fuel mixture."

Many common fuels contain combustible hydrogen, which upon burning, forms water vapor. Normally, as the products are being cooled, part of this water vapor condenses, giving up its latent heat. The amount of heat that may be removed, then, depends upon the amount of water vapor condensed. This amount of water vapor that condenses is a function of the following:

a. Temperature of the original mixture
b. Barometric pressure
c. Relative humidity of the air
d. Excess air used

It may be seen that there is an infinite number of heating values of a fuel, according to the definition given in the first paragraph. Using this definition, there is, however, a maximum heating value of a fuel and also a minimum heating value. The minimum heating value may be obtained if sufficient excess air is used so that there will be *no* condensation of the water vapor of combustion. This heating value is the "lower" or "net" heating value. The maximum heating value of a fuel is obtained when the air contains sufficient moisture to completely saturate the products of combustion. In this case, all of the water vapor of combustion will condense. This is the "higher" or "gross" heating value.

The difference between the higher and the lower heating values is a constant for any particular fuel.[1] In the case of constant pressure combustion, this difference is the latent heat of the water vapor of combustion (taken at the temperature of the original mixture). For constant volume combustion, the difference is the internal energy of vaporization.

At 75 F the latent heat of water vapor is 1050 Btu per lb and the internal latent energy is 991 Btu per lb. These figures vary slightly with temperature[1] but as the latent heat of the water vapor is only a small part of the heating value of a fuel, this variation with temperature may be neglected and the difference between the higher and the lower heating values taken to be 1050 Btu per lb of water vapor resulting from combustion. This figure is for constant pressure combustion. For constant volume combustion, the figure 990 Btu is to be used.

[1] Before combustion, the air-fuel mixture possesses a definite amount of both chemical and molecular energy. During combustion, new substances are formed and chemical energy is transformed into molecular energy (heat). Generally, the molecular energy of the products is not the same as the molecular energy of the mixture, even at the same temperature. The heat that is removed is equal to the algebraic sum of the chemical energy of the fuel and the net change in molecular energy. The difference between the molecular energy of products and mixture varies so slightly with temperature that it is generally neglected. If this difference is desired, the molecular energy of the mixture and the products may be calculated knowing the specific heats (See Bulletin 139, University of Illinois, by Goodenough and Felbeck).

The representation of the process of combustion is shown on the accompanying T-ϕ diagrams. Point 1 represents the charge. It is assumed that a spark raises an infinitesimal portion of the charge up to its ignition temperature. This portion of the charge then burns, heating more of the charge up to its ignition temperature. This process continues until (if the effects of dissociation be neglected) the fuel is completely burned and the products exist at condition 2. It is also assumed that the combustion 1–2 is adiabatic. In order to cool the products down to the original temperature, heat must be removed from the products. This heat which is removed is the heating value of the fuel and is represented by the cross-hatched areas on the T-ϕ diagrams. Line 2–3 may lie to the left of or to the right of line 1–2, or may cross it depending on the nature of the fuel and the products. Point 3 represents the dew-point of the products. Point 4 is the final condition of the products.

Determination of Heating Value

Most of our fuels are solids or liquids. Their heating values generally are determined in the bomb calorimeter. If a few drops of water are added to the bomb before sealing, this water will saturate the space inside the bomb and all the water vapor of combustion will condense. As the combustion has been at constant volume, this determination is, directly, the "higher heating value at constant volume."

The heating values of the gaseous and sometimes the lighter of the liquid fuels are determined in the gas calorimeter. This combustion is of the flow type and is at constant pressure. Normally, only a portion of the water vapor formed will be condensed. The heating value thus obtained is a heating value at constant pressure, and is a heating value intermediate in amount between the higher and the lower heating values. When the humidity of the entering air is high and the fuel is rich in hydrogen, the heating value obtained approaches the higher value. If the entering air is relatively dry and the hydrogen content of the fuel is low, the heating value determined in the gas calorimeter approaches the lower value. Normally, however, an appreciable error is caused by using the gas calorimeter determination for either the higher or the lower heating values.

Although it is possible to measure the higher and lower heating values as mentioned above, it is much simpler for constant pressure combustion to calculate these values from the gas calorimeter determination. The weight of water vapor of combustion is easily calculated from a knowledge of the hydrogen content of the fuel. In the gas calorimeter, the amount of condensate is measured. By subtraction, the amount of water vapor of combustion not condensed is easily found. The lower heating value at constant pressure is equal to the gas calorimeter determination minus the product of 1050

and the pounds of water vapor of combustion condensed. The higher heating value at constant pressure is equal to the gas calorimeter determination plus the product of 1050 and the pounds of water vapor of combustion not condensed.

Heating Values at Constant Pressure and Constant Volume

The difference between the heating value at constant pressure and that at constant volume is very small and is generally neglected. However, for refined calculations, it may be desirable not to neglect this difference.

If the pressure is held constant, and the final volume of the products is greater than the volume of the original mixture, then work has been done to push the atmosphere out of the space occupied by the additional products volume. As this work is done by the combustion, less energy is available to be removed as heat. The heating value at constant pressure is then less than the heating value at constant volume. Likewise, it may be shown that in case the final volume of the products is less than the volume of the original mixture, the heating value at constant pressure is greater than the heating value at constant volume.

From the combustion equation: $C + O_2 = CO_2$, it may be seen that the volume of oxygen is replaced by an equal volume of CO_2. If the carbon comes from a liquid or solid fuel, its original volume is negligible in comparison to the volume of gaseous oxygen used and the volume of the gaseous products formed. Hence, when carbon burns under such conditions, the volume of the products formed by burning the carbon is practically the same as the volume of the original mixture. Whatever change in volume there may be is then due to the combustion of hydrogen.

From the combustion equation: $2H_2 + O_2 = 2H_2O$, it may be seen that one volume of oxygen is replaced by twice its volume of H_2O. Here, again, if the hydrogen comes from a liquid or solid fuel, its original volume is negligible as compared to the volume of the gases present.

If there is no condensation of the water vapor (as in the case of a lower heating value determination), the volume of the products, resulting from the combustion of hydrogen in a liquid or solid fuel, is greater than the original volume. The difference in volumes is equal to the volume of the oxygen used to burn the hydrogen.

If there is complete condensation of the water vapor, (as in case of the determination of higher heating value) since the volume of water in the liquid state is exceedingly small, the volume of the products is less than the volume of the original mixture. The difference in volumes is equal to the volume of the oxygen used to burn the hydrogen.

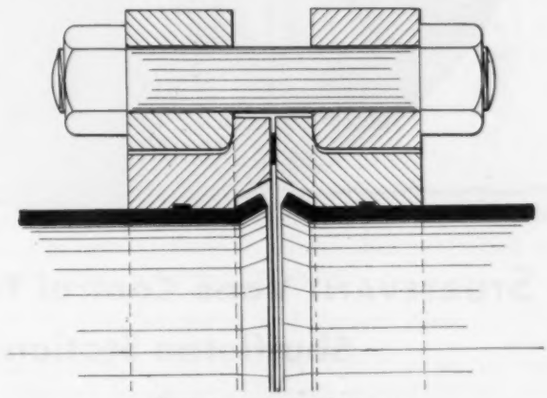
At 75 F and standard atmospheric pressure, the work done due to the change in volume is 29.4 Btu per lb of water vapor of combustion.[2] This figure changes slightly with a change in temperature but may be taken as 30 Btu.

Following the above reasoning, it may be said that the higher heating value at constant pressure is greater than the higher heating value at constant volume by 30 Btu per lb of water vapor of combustion and that the lower heating value at constant pressure is less than the lower heating value at constant volume by the same amount.

[2] To form one pound of water vapor requires eight-ninths of a pound of oxygen. The volume of this oxygen at 75 F and 14.7 lb per sq in. abs is 10.82 cu ft. In case the higher heating value of the fuel is being determined, the water vapor condenses and the volume of the products is 10.82 cu ft less than the volume of the mixture. As the amount of water vapor formed is twice the volume of the oxygen that goes to form the water vapor, in the case of the lower heating value of the fuel, no condensation takes place and the increase in volume, because of combustion, is 10.82 cu ft per lb of water vapor. In either case, then, there is a change in volume during the constant pressure combustion of 10.82 cu ft per lb of water vapor. This change in volume generally takes place at atmospheric pressure. The heat equivalent of this work done during the change in volume is 29.4 Btu per lb of water vapor, using standard atmospheric pressure.

Joint for Field Assembly

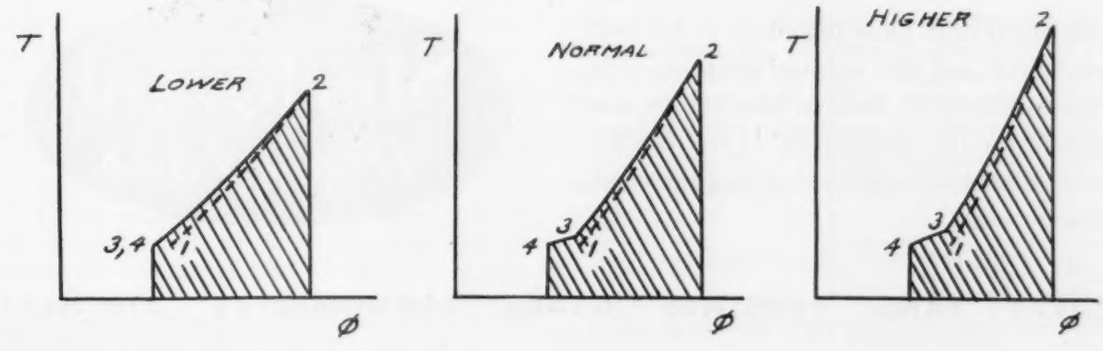
The sketch shows a flange which may be used in place of the lap joint (or Van Stone) flange. It is made in two sections, the center section having the pipe rolled into it, thereby permitting the flange to be attached



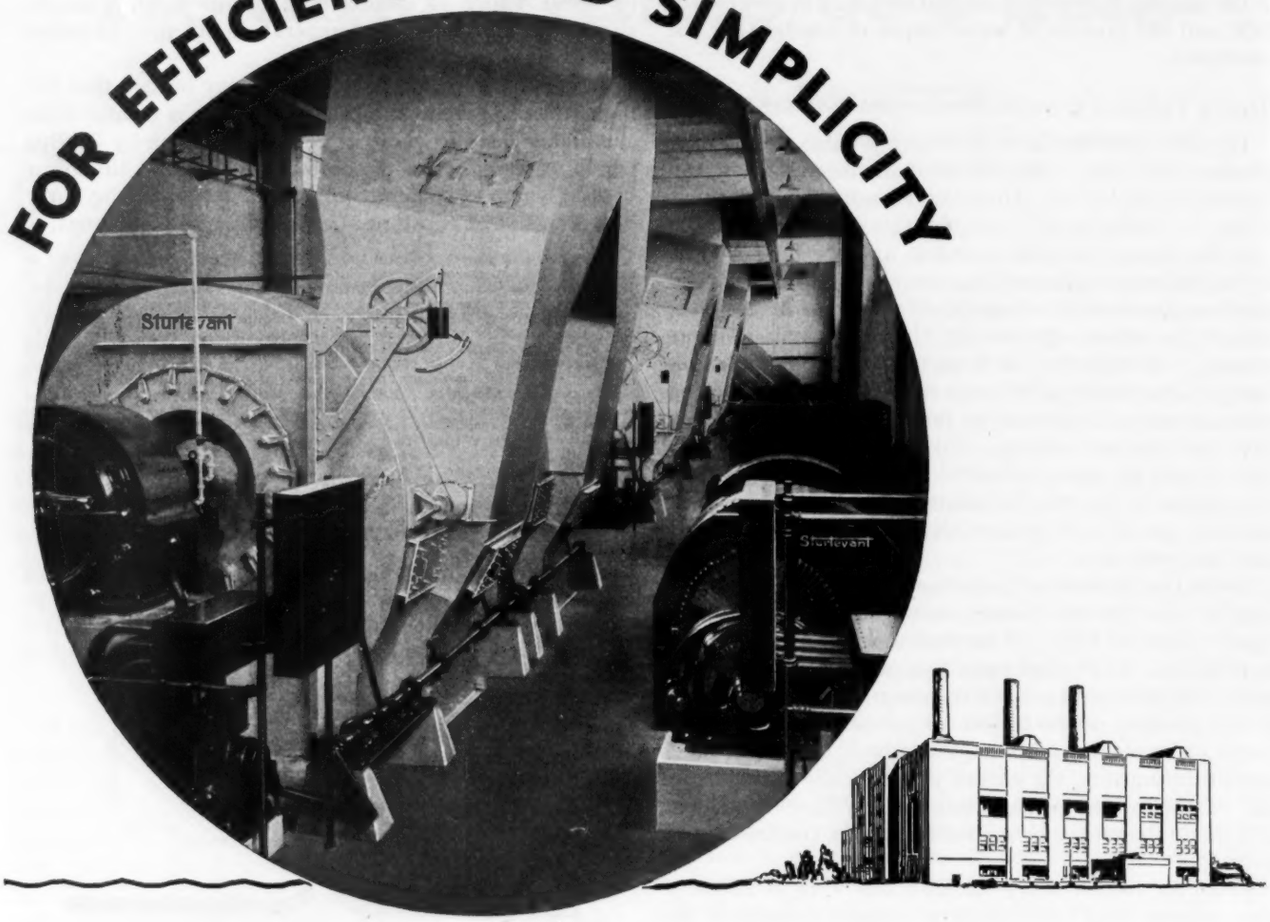
Cross-section through joint

either during erection or in the shop; whereas, the attaching of a lap joint flange is strictly a shop construction job.

The present standard is a one-piece flange which may be attached by rolling during erection or in the shop, but careful attachment is required so that the bolt holes will match with the companion flange. The arrangement here shown permits easy alignment of the bolt holes and should result in saving of time.



FOR EFFICIENCY AND SIMPLICITY



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Rolling-In of Boiler Tubes*

By F. F. FISHER and E. T. COPE
The Detroit Edison Company, Detroit, Mich.

This paper presents the results of a study of the expanding of boiler tubes and proposes a method which, over a five-year period, has produced uniform joints of optimum strength. In this method the severe cold working of the tube and drum metal, because of excessive expanding of the tubes, has been either avoided entirely or reduced to a minimum.

KNOWLEDGE of what constitutes a satisfactory rolled joint is now lacking. Once this knowledge is available and the correct procedure for rolling the joint has been established, the production of joints of maximum strength and tightness could be controlled. If the tubes could be machined to fit into carefully tooled tube holes, or if the tube ends could be shrink-fitted into the holes, the problem would be relatively easy. But liberal clearances must be allowed to permit easy introduction of the tubes into the holes, particularly in tight places, of which there are many in a modern large-capacity boiler. Commercial practice and the demand for low-cost production puts precise machining out of the question. On the other hand, if the differences in diameters between the tubes and tube holes were constant to a micrometer tolerance and the tube-wall thickness did not vary, the problem of securing uniform joints would be relatively simple. Also, if the surfaces of tube and tube hole which are to produce the joint were of uniform and standard finish, the production of uniformly tight and strong joints would not be so difficult. But when joints are to be made between the surfaces of tube ends and tube holes in which the clearance may have any value from ten-thousandths to sixty-thousandths of an inch in a bank of tubes, where the tube holes are reamed to commercial finish yet the tubes are covered with mill scale or are indifferently cleaned, one should not be surprised if a considerable percentage of the joints shows leaks when the assembled structure is subjected to a hydrostatic-pressure test. Neither should one be surprised if the rerolling operation causes leaks in joints accepted on the first hydrostatic test, nor that such rejoints fail after a comparatively short period of service.

The production of a joint by expanding a tube into a tube hole entails the execution of two distinct phases of the rolling-in operation. The first consists of stretching the tube wall until there is contact between the outside surface of the tube and the inside surface of the tube hole. A joint does not begin to exist until this contact has occurred. As already noted, the difference in diameter of the tube and the tube hole is by no means constant in any group of prospective joints. Therefore, the amount of expanding of the tube necessary to produce contact between tube wall and tube hole may vary widely from tube to tube. Consequently, this fact must be taken into account when producing a joint. The second phase of the rolling-in operation consists of giving the tube wall further permanent stretch, thus pressing the outside surface of the tube against the inside surface of the tube hole. This pressure alone is the source of fluid tightness in the joint. Also this pressure, coupled with the friction between the two metal surfaces, is the source of the strength of the joint which holds the tube in the tube hole when pressure is applied within the boiler. Since the pressure between the two surfaces is the only variable in any given case entirely within the control of the mechanic doing the assembling, it might be at once concluded that the greater the expansion the better the joint. That this is not true has been demonstrated by tests which show that both the tube wall and the metal surrounding the tube hole are subjected to severe cold working when excessive expansion is practiced. When a tube must be replaced in a tube hole which has been heavily over-expanded, the hole is badly distorted and should be re-reamed to true it up and to remove the metal which was overstressed at the previous rolling.

The Function of the Bulge and Flare

The opinion is held by boiler men that the tightness and strength of the joint depends in part on the bulge and the flare made during the expanding operation. It is true that the flare will prevent the tube from slipping out of the tube hole. When the tube is rolled-in, the backing out of the expander pushes the flare a few thousandths of an inch away from the tube sheet so that the flare does not contribute to the tightness or holding strength of the joint. Also, in many cases the flare is not correctly rolled and its effect on holding strength is therefore doubtful. In the case of flat tube sheets, the initial expanding of both bulge and flare will produce contact completely around the tube. On the other hand, in joints expanded into curved tube sheets excessive work on the flare is necessary to produce contact all around the tube. This produces a rounded edge in the tube hole which makes very difficult the refitting of a new tube in case of replacement. The flare does perform an important function in providing a smooth entrance to the tube which reduces the resistance to flow.

Requirements for an Ideal Joint

The formation of an ideal joint by rolling-in requires:
1. A device for expanding the tube so that it is

* Excerpts from a paper to be presented at the Semi-Annual Meeting of the American Society of Mechanical Engineers, Cincinnati, Ohio, June 18 to 21, 1935. Contributed by the Power Division.

cylindrical at all times during the rolling-in operation.

2. A means by which the completion of the first phase of the rolling-in will be indicated definitely. This anticipates a mechanical, a magnetic, or an electrical device for positively indicating the establishment of a firm contact between the outside surface of the tube and the inside surface of the tube hole.

3. A means for indicating the amount of deformation of the metal surrounding the tube hole. This metal should not be stressed beyond its elastic limit.

A method of tube expanding based on these requirements should produce fluid-tight joints which show the optimum strength to resist destruction when subjected to fluid pressure. Furthermore, it has been well established that corrosion fatigue occurs at points of high stress concentration. The metal of tubes and tube sheet surrounding the holes in boilers in which the tubes have been heavily over-rolled should be an ideal point for the beginning of this form of failure.

Conventional Methods of Tube Expanding

Three methods of tube expanding are generally accepted. These are the tube-bulge method, the uniform-expander-entrance method, and the measured-energy-input method. These will be reviewed briefly and their limitations pointed out. In the tube-bulge method, a few tubes in a bank, used as samples, are expanded until their outside diameters are increased a definite amount ($^1/_{32}$ in. usually) over the nominal tube-hole diameter. This measurement is made immediately next to the tube sheet or drum on the gas side in a water-tube boiler and the water side in a fire-tube boiler. The amount of tube bulge is measured by a gage of fixed opening. The expanding or rolling operation is carried out until this outside gage fits the bulge of the tube. After the operator gets the "feel" of rolling-in these samples, he proceeds to roll-in the remainder without measurement.

In the second method of tube expanding, the tool is entered a fixed distance into all the tubes in a given bank. This distance is determined by trial on a few tubes and the stop is set. In the uniform-energy-input method all joints are rolled-in with a consumption of a given amount of energy expressed in watthours or horsepower-hours.

In these methods of tube expansion there is no way of knowing definitely when the tube surface contacts the tube hole. Also, there is no way of knowing how much the tube is expanded after contact occurs.

The tube-bulge method of expansion does not meet the second and third requirements of the ideal expansion method. If the joints are assembled by the uniform-expander-entrance method, in which no exact account is taken of the variation in clearance between tube and hole, and no allowance is made for the variation in tube-wall thickness, it is obvious that the resulting joints would not be expanded uniformly. If by chance, resulting from random choice of tubes, the smallest tube having the thinnest wall has been expanded into the largest hole, the resulting joint would be very different from the one resulting from expanding the largest tube having the thickest wall into the smallest hole. In the first case the tube might have been expanded only enough to contact the tube hole, whereas in the second case the joint would have been heavily over-expanded, resulting in severe cold working of the metal of tubes and tube sheet and the setting up of points of very high stress concentration. This second method, therefore, also falls short of meeting the requirements of the ideal method of tube expanding.

In the uniform-energy-input method no account is taken of the influence of differences in tensile strength of the metal of the tubes and sheets, differences in clearance between tube and tube hole, nor the condition of the rolling tool. When the self-feeding expander is used, the power required to flare the tube is at maximum at the same instant as that required for completing the rolling-in operation of the joint itself. The flare does not constitute an essential portion of the joint and the energy required to complete the flare cannot be separated from the total. This method also falls far short of meeting the requirements of the ideal joint.

The shape of the entering ends of the expanding-tool rollers is a matter of considerable importance. Since the metal on the inside of the tube wall is cold worked, it is of the highest importance that this cold working should take place with the least possible disturbance of the metal surface. If the entering ends of the rolls are not sufficiently rounded they leave a sharp shoulder at the inner end of the rolled portion. This produces an ideal starting point for cracks or corrosion, as shown by numerous tube failures which have been investigated. With self-feeding expanders, especially when used for rolling-in tubes into thick sheets (such as $1^1/_4$ in. and upward), the metal on the inside of the tube is plowed up by one roller and then rolled down by the succeeding ones. This leaves a spiral mark on the inside of the tube. It is usually not noticeable upon casual inspection, yet constitutes an excellent starting point for corrosion. To correct this condition the boiler erectors in the authors' company have ground the entering ends of the rollers of their expanders to a five-inch radius. A certain amount of cold working takes place, but instead of the metal being plowed into a sharp crest it is moved ahead of the rollers in the form of a gentle undulation. No roller scars are visible on the inside surface of the tubes.

The Elongation Method of Tube Rolling

The elongation method of tube rolling, as developed by the company with which the authors are associated, more nearly fills the specifications for an ideal method than does any one of the other methods noted. In this method advantage is taken of the fact that the tube is loose in the tube hole until the first phase of the rolling-in is completed. It further takes advantage of the fact that during the expanding operation the wall of the tube within the tube sheet is thinned. The metal is squeezed between the expanding tool and the surface of the tube hole and is forced to flow axially. This moves the tube axially a measurable amount, which is a function of the degree of the expansion. The only extra tool required by this method is a dial indicator fitted with the proper size clamp, so that the indicator may be readily attached to the tubes. The tube is inserted into its tube hole and manually held in place. The clamp extends half way around the tube and bears at three points to prevent rocking. The end of the shaft of the dial indicator rests on the tube sheet or drum. The expanding operation proceeds, using a "parallel" expanding tool. During the first operation the needle of the dial indi-

cator vibrates until the tube has been stretched into circumferential contact with the tube hole. At the instant of this contact the needle comes to rest, indicating that the first operation has been completed, and item two of the ideal method of expanding has been met. Continued expansion further stretches the tube wall into firmer contact with the hole and squeezes it so that axial flow occurs. This axial flow causes movement of the dial-indicator needle. The amount of movement of the needle necessary to produce the best joint has been established by tests. It appears that the most satisfactory joint is produced when the elongation is about 0.020 in.

Effect of Lengthening the Tubes Caused by Rolling-In

The tests which established the elongation method of rolling-in tubes, showed that the tube is lengthened a measurable amount by the rolling operation. The more heavily the tube joint is rolled-in, the greater the lengthening of the tube. If adjacent tubes in a drum or tube sheet are rolled-in to different elongations, the difference in lengthening sets up considerable thrust on the tube which has been rolled the least, or compression on the tube which has been rolled the most. This compression may lead to the bowing of the more heavily rolled-in tube with the possibility of failure because of interference. If it were possible to roll-in all the tubes of a given bank or bundle simultaneously and equally, there would be no difference in lengthening of adjacent tubes. But at present tubes are rolled-in one at a time. The elongation given each tube except the first, imposes a thrust on all tubes that have been previously rolled-in. The presence of accumulation of thrust is especially evident in straight "tack tubes." That this is true is shown by the failure of tack-tube joints during assembling of the boiler, and perhaps more frequent failure after the boiler has been in service for some time. The actual value of this axial loading is a difficult matter to calculate, because of the shapes and arrangements of the tubes in any given boiler. An approximation has been made, however, by actually weighing the axial thrust during the rolling-in operation. This was carried out by having the free end of a short tube, which was being rolled into a 10-in. square plate, exert its axial thrust against the ram on an hydraulic jack. The base of the jack and the plate were rigidly joined together. The hydrostatic pressure shown by the gage on the jack was multiplied by the area of the jack plunger to give the value of the thrust. While this test is not presumed to reproduce the conditions occurring during the erection of a boiler, yet it does indicate the possible magnitude of the thrust.

The accumulation of thrust, if not controlled, often results in the bulging of the tube sheets, the raising of steam drums off their supports during erection or even the rupture of tubes. Control of cumulative thrust applied to boilers having drums may be effected by either of two procedures. In both cases tack tubes are installed first. They are fully rolled-in at one end and partly rolled-in at the other. Next, the remaining tubes are fully rolled-in at one (usually the upper) end and partly rolled in (usually to 0.005 in. elongation) at the other end. In the first procedure, the partly rolled-in ends are then fully rolled-in proceeding along the length of the drum. In the second procedure, tack tubes are rolled-in as in the first procedure. All remaining tubes are fully rolled-in at one end (usually the upper end), the remaining joints are then rolled-in, starting at the middle of the length of the bank and rolling tubes to full elongation toward the end of the bank. This divides the amount of accumulated elongation and the consequent thrust in half. In long banks, the rolling-in of the remaining tubes is carried out by dividing the length of the bank into four parts and rolling the tubes in each fourth of the length separately. Any of these methods reduces the amount of accumulated thrust and makes less likely the failure of the joints from this cause.

Fuel and Power Papers at A.S.M.E. Semi-Annual Meeting

The technical program for the Semi-Annual Meeting of the American Society of Mechanical Engineers, at Cincinnati, Ohio, June 18–21, contains the following papers of interest to power men:

"Division of Load among Generating Units for Medium Cost," by J. E. Mulligan.

"Leakage of Steam through Labyrinth Seals," by A Egli.

"Steam Turbine Bearing Losses and Vacuum Corrections," by Linn Helander.

"Principles Underlying Rational Solution of Automatic Control Problems," by S. D. Mitereff, Jr.

"Application of Mutual Point Theory to Pipe Stream Calculations," by S. W. Spielvogel.

"Rolling-In of Boiler Tubes," by F. F. Fisher and E. T. Cope.

"A New Basis for the Rating of Roller Chain Drives," by G. M. Bartlett.

"Theory and Design of Pivoted Motor Drives," by R. R. Tatnall.

"Radiation Intensities and Heat Transfer by Radiation in Boiler Furnaces," by H. O. Croft.

"A Simpler Type of Slag Furnace Bottom," by J. H. Strassburger.

"Possibilities of Pulverized Coal for Small Boilers," by James W. Armour.

The steam power papers are scheduled Thursday morning and afternoon, the fuels papers for Friday morning and afternoon, and the power transmission papers for Thursday afternoon.

E.E.I. to Meet at Atlantic City

The Third Annual Convention of the Edison Electric Institute will be held at Atlantic City, N. J., on June 3 to 6. Headquarters will be at the Traymore Hotel. This convention was originally scheduled for Washington, D. C., but upon the expressed wish of members the place of meeting was changed. The sessions will be open and will be addressed by executives of the industry as well as several nationally known leaders in other fields. One of the subjects scheduled for discussion is the report of the Federal Trade Commission's utility investigation and another is plant modernization.

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Stress Relief of Fusion-Welded Pressure Vessels*

By D. S. JACOBUS, President
American Welding Society

THERE is no subject bearing on the construction of fusion-welded pressure vessels on which there is such a wide variation of opinion as the conditions which make it necessary to stress relieve the joints. The A.S.M.E. Code requires that the stresses be relieved in certain cases by heating uniformly to at least 1100 F, and up to 1200 F, or higher, if this can be done without distortion, and holding the vessels at that temperature for a period proportioned on the basis of at least one hour per inch of thickness. The Code covers the welding of plain carbon steels in which the carbon content does not exceed 0.35 per cent. All welded drums for power boilers and all pressure vessels employed in the most dangerous service are required to be stress relieved, but the Unfired Pressure Vessel Code sanctions the use of quite a wide range of fusion-welded vessels without stress relief.

The temperature specified for stress relieving the welds does not refine the grain structure. In vessels made of alloy steel or in which the carbon limit exceeds that specified in the Code, it is necessary in many cases to refine the grain adjacent to welding by heating the vessels to above the critical temperature after welding. The remarks which follow apply to the stress relief of vessels constructed of plain carbon steel in accordance with the rules of the A.S.M.E. Code where the carbon content does not exceed 0.35 per cent and may not apply to vessels constructed of other grades of steel.

The A.S.M.E. Unfired Pressure Vessel Code requires unfired pressure vessels, which are to be used under the most exacting service conditions, to be stress relieved, and others for a limited field of service to be stress relieved when the shell thickness for a given diameter exceeds a certain figure. Vessels of the latter class are required to be stress relieved where both the wall thickness is greater than 0.58 in. and the shell diameter less than 20 in., and for all other wall thicknesses and shell diameters where the ratio of the diameter to the cube of the shell thickness is less than 100, and in all cases where the shell thickness is over $1^1/_2$ in.

The A.S.M.E. Unfired Pressure Vessel Code sanctions the use of unfired pressure vessels of the latter class for storing gases other than those of a lethal nature. Where water or other liquid is present in the vessel the pressure for a vessel that may be used without stress relief is limited to 400 lb per sq in., and the temperature to 300 F. The object of these limitations where the vessels contain liquids is to insure safety for types of vessels where the energy developed in the case of an explosion by the heated liquid has led to disastrous results. The A.S.M.E. Code is more liberal in its stress relief requirements than any other Code that I know of. For example, the specifications of the Bureau of Engineering of the U. S. Navy call for stress relieving all fusion-welded pressure vessels, and the "Tentative Requirements of Lloyd's Register of Shipping for Fusion-Welded Vessels Intended for Land Purposes" call for heat treating all vessels subject to internal steam pressures above 50 lb per sq in., and other vessels, depending on the service for which the vessels are intended.

One of the objects of the rule given in the A.S.M.E. Boiler Code was to exempt certain vessels from the requirements of stress relief where it would be impossible to stress relieve the vessels. The vessels in mind were those built in the field having large diameters, say 30 ft or more, where it would be impossible to stress relieve the vessels as a whole and where there would be more flexibility than in a smaller vessel of the same plate thickness.

The rule exempting certain unfired pressure vessels from stress relief which was finally embodied in the Unfired Pressure Vessel Code was prepared jointly by the American Welding Society and the A.S.M.E. Boiler Code Committee. It was published in *Mechanical Engineering*, the official organ of the American Society of Mechanical Engineers, with a request that criticisms or suggestions be submitted to the Boiler Code Committee. No criticisms or suggestions were received before including the rule in the Unfired Pressure Vessel Code, whereas there has been considerable discussion as to the exactness of the rule since its inclusion and the Boiler Code Committee has been requested to provide a more liberal rule.

Many investigations are in progress and much has been published on the strains and the corresponding stresses due to welding. It has been shown that welding a seam in a pressure vessel may produce elongations in the plate adjacent and at right angles to the weld which will be two or more times as great as that required to produce a stress equal to the yield strength of the material. It has also been shown that the residual strains after the welding, both at right angles and parallel to the weld, may be in the neighborhood of those corresponding to the yield strength of the plate. It is well known that in fusion welding a pressure vessel it will at times rupture due to the strains produced by the welding before the application of the hydrostatic test in the shop, all of which shows that the strains due to the fusion welding are of great magnitude. The question arises as to the effect of these strains should the vessel be placed in service without stress relief.

There is a feeling on the part of some that if a vessel is placed in service after being subjected to the usual hydrostatic tests that the stresses will gradually diminish due to the creeping of the material and safety will result

* From address on Standards and Codes for Fusion Welding presented at Meeting of Local Sections of American Welding Society, American Society of Mechanical Engineers and American Society for Metals, Detroit, Mich., Apr. 17, 1935.

through the readjustment of the stresses, provided the welds are sound and the weld metal of as uniform and as good quality as the plate.

Vessels tested by subjecting them to pulsating pressures have ruptured in the metal of the plate parallel to the weld at lower stresses than correspond to the strength of the material. It has been shown that this action may come through the stresses adjacent to the weld produced by the welding, as these stresses added to the hoop stress produced by the hydrostatic pressure may correspond to or exceed the endurance limit of the material. For certain types of service, therefore, there would seem to be no question but that it is well to stress relieve all fusion-welded vessels.

A most important feature that must be considered in deciding whether a vessel should be stress relieved is the chance that the weld will not be as uniform and as strong as the parent plate. If portions of the welded joint are not thoroughly fused, experience has shown that intermittent stresses due to variations in temperature or pressure will lead to cracks starting at the unfused portions and extending so that danger may result. Stress raisers of the sort due to imperfections in the weld are something that must be given most serious consideration and in case of a doubt those responsible for the formulation of safety codes naturally lean toward conservative rules.

Rapid Advances Make Caution Advisable

The results secured in long service are the best measure of safety. It is difficult, however, to formulate rules based on the results secured in service where the art is advancing as rapidly as in the case of fusion welding and where defects may be developed after many years of use. Again, the stresses depend in a great measure on the method used in welding, and many variables are involved. We must not be misled through the rapid advances that have been made in the last few years into thinking that we know all about fusion welding. As I have said on other occasions, I do not believe we have proceeded over 25 per cent of our way and it is certainly much better to advance carefully rather than to make mistakes for which we may be sorry.

All that I have said bears on fusion-welded pressure vessels. The question naturally arises as to the use of fusion welding in other fields, such as in building, bridge and ship construction, where it would be impossible to stress relieve most of the joints. Great progress has been made in this type of welding and the record has been exceptionally clean in regard to failure in service. We therefore should not close our minds to providing more liberal rules for the stress relief of unfired pressure vessels if reliable information is secured which will warrant this being done with safety.

Bursting tests of vessels under hydrostatic pressure made in the ordinary way do not give data on which to base a rule for stress relief, as the residual stresses due to the welding have little or no effect on the bursting strength, whereas tests under intermittent pressures are especially valuable for the purpose. Such tests were proposed a long time ago by the American Welding Society and the Boiler Code Committee in working up a series of tests to be made at the Bureau of Standards in Washington. The tests were designated at the time as "breathing tests" in which the vessels were to be subjected to pressures alternating from about zero to $1^1/_2$ times the allowable working pressure. These suggested tests were not made at the Bureau of Standards but The Babcock & Wilcox Company made tests along these lines under the supervision of Professor H. F. Moore. These tests did much in establishing the reliability of fusion welding and they are now regarded as accelerated service tests. Tests of the sort should be sufficiently inclusive as a few tests under a given set of conditions may not solve the problem.

Local stress relieving such as heating the area around a nozzle may set up objectionably high stresses in the shell of a vessel adjacent to or around the part that has been stress relieved. Where a vessel is stress relieved in two heats on account of it being longer than can be placed in the stress relieving furnace, there also may be objectionable stresses should the temperature gradient be too high in the portion between the heated and cooled part of the shell. This feature in stress relieving a vessel in two heats was provided for in the preparation of the Joint API-ASME Code for Unfired Pressure Vessels for Petroleum Liquids and Gases, which includes the requirement that the temperature gradient for the part in question shall not exceed 200 deg. F. per foot along the shell.

There are so many features of stress relief that have not been settled that some users of pressure vessels require all vessels to be stress relieved when the wall thickness is, say, $^3/_4$ in., or over, even though no stress relief is demanded by the A.S.M.E. Code.

My own Company has conducted researches at great expense to investigate the strains produced in fusion welding, which will be published on their completion. These have convinced us that to secure maximum reliability and safety all vessels should be stress relieved after welding. It is our practice usually to stress relieve all vessels even though some are exempted from stress relief by the A.S.M.E. Code.

There is a lot to learn on this subject and while we should be looking forward to the possibility of using more liberal rules, we should make sure not to proceed unless reliable scientific data and facts show that the revised rules will be safe.

Approves Huge Tidal Power Project

The PWA has tentatively approved the allotment of thirty million dollars to construct the Passamaquoddy tidal power project in Maine. This scheme for utilizing the twenty-seven foot tides in the Bay of Fundy was originally proposed by Dexter S. Cooper seven or eight years ago. It involved the building of a series of dams across the islands of Passamaquoddy Bay and Cobscook Bay, the installation of five 41,000-hp pumping units to pump water up into the reservoirs and the development of 464,000 hp initially. Mr. Cooper applied to the Federal Power Commission for a permit in 1929. While the installation was feasible from a construction standpoint, it was not considered economically justifiable and it could not be financed.

Now the PWA proposes to construct an aluminum plant and a stainless steel plant in order to provide an outlet for the power.

Dissociation of Products of Combustion

By WM. L. DEBAUFRE,

Chairman, Department of Engineering Mechanics, University of Nebraska

The present article includes tables and curves by means of which dissociation of products of combustion may be calculated and corrections made to the thermal properties of products of combustion at high temperatures. Thermodynamic relations and experimental data show that actual conditions closely correspond to results calculated in this way. In special cases, however, dissociation of molecular hydrogen into atomic hydrogen, association of nitrogen and oxygen into nitrous oxide, etc., may be sufficient to affect the results. For a discussion of these effects and of "the maximum temperatures and pressures attainable in the combustion of gaseous and liquid fuels," the reader is referred to University of Illinois Bulletin No. 139.

COMBUSTION is a chemical process. Most fuels consist of a mixture of numerous chemical compounds of hydrogen, carbon, sulphur, oxygen and nitrogen. In the process of combustion, these chemical compounds are broken down into their elements, and the combustible elements, hydrogen, carbon and sulphur, then unite with oxygen from atmospheric air to form products of combustion. The combustion process itself will not be discussed in this article, which will be confined to the thermal properties of products of combustion, particularly as affected by temperature.

In the two articles entitled "Typical Solid and Liquid Fuels" and "Typical Gaseous Fuels" in COMBUSTION for August and December 1931, respectively, a method of calculating the composition of products of combustion from the chemical analysis of a fuel was described and illustrated. Complete combustion was assumed. The products of combustion then comprise:

Moisture,	H_2O
Carbon dioxide,	CO_2
Sulphur dioxide,	SO_2
Oxygen,	O_2
Nitrogen,	N_2

The sulphur dioxide is generally small in amount and for thermal purposes may be treated as carbon dioxide.

We generally think of combustion reactions as proceeding to completion if sufficient oxygen is present for the purpose. The chemical reaction of hydrogen combining with oxygen may, however, take place in the opposite direction. That is, moisture may dissociate into hydrogen and oxygen. The chemical equation

$$H_2O \rightleftharpoons H_2 + {}^1/_2\, O_2 \qquad (1)$$

is often written with double arrows instead of an equality sign to indicate that this chemical reaction can proceed from left to right as well as from right to left.

Also, carbon dioxide may dissociate into carbon monoxide and oxygen. The carbon monoxide may then dissociate into carbon and oxygen. The latter dissociation, however, is ordinarily so slight that the former only need be considered. For dissociation of carbon dioxide, we therefore have

$$CO_2 \rightleftharpoons CO + {}^1/_2\, O_2 \qquad (2)$$

As to whether the preceding chemical reactions will proceed in one direction or the other, depends upon the relative proportions of the various kinds of molecules present and the temperature and pressure of the gaseous mixture. At moderate or low temperatures and except at extremely low pressure, these reactions tend to proceed from right to left until very slight traces of either hydrogen or carbon monoxide remain uncombined with oxygen. That is, with sufficient oxygen present, combustion is practically complete. In industrial furnaces, we are not concerned with extremely low pressures, but we are sometimes concerned with temperatures exceeding 3000 F. At these temperatures, appreciable dissociation of moisture and of carbon dioxide exists.

At any particular temperature of a given gaseous mixture, there is an equilibrium condition which would persist indefinitely with certain fractions of moisture and of carbon dioxide dissociated. With a greater or less fraction of either dissociated at the same temperature, equilibrium does not exist but there is a driving force which causes the chemical reaction to proceed until equilibrium is reached.

The fractions of moisture and of carbon dioxide dissociated under equilibrium conditions at any particular temperature can be calculated by means of a mathematical expression derived from thermodynamics with the aid of a few experimental results at one or more temperatures. To derive this mathematical expression, we assume combustion to be complete and then that dissociation occurs at constant temperature. Thus,

for complete combustion with no dissociation, we might have in the products of combustion:

m lb-moles H_2O
k lb-moles CO_2
o lb-moles O_2
n lb-moles N_2

$m + k + o + n = g$ lb-moles gaseous mixture

At any instant, let the fraction of moisture dissociated be denoted by x and the fraction of carbon dioxide dissociated be denoted by y. Then, after dissociation, we would have:

$(1\text{-}x)\ m$ lb-moles H_2O
xm lb-moles H_2
$(1\text{-}y)\ k$ lb-moles CO_2
yk lb-moles CO
$o + xm/2 + yk/2$ lb-moles O_2
n lb-moles N_2

$g + xm/2 + yk/2$ lb-moles gaseous mixture

Suppose that as the result of adding a small quantity of heat dQ, the dissociation of moisture increases by dx and the dissociation of carbon dioxide increases by dy. Let the corresponding increase in entropy of the gaseous mixture be dS at constant absolute temperature T. In general, the heat added dQ is not equal to $T\,dS$. The latter is equal to the heat added at constant temperature only when the gaseous mixture is in thermal equilibrium with its surroundings while receiving heat therefrom. When equilibrium does not exist, there is a tendency for conditions to change until equilibrium is reached. The difference $dQ - T\,dS$ is then a measure of the driving force of the chemical reaction and will be denoted by dF, where F is known as the free energy of the gaseous mixture. Since dF, dQ and dS all correspond to changes of dx in the dissociation fraction of moisture and of dy in the dissociation fraction of carbon dioxide, we may write: For dissociation of water vapor,

$$\frac{dF}{dx} = \frac{dQ}{dx} - T\frac{dS}{dx} \qquad (3)$$

For dissociation of carbon dioxide,

$$\frac{dF}{dy} = \frac{dQ}{dy} - T\frac{dS}{dy} \qquad (4)$$

Combustion in furnaces usually occurs at constant pressure. We will therefore assume dissociation to proceed at the constant total gas pressure of P atmospheres rather than at constant volume. At constant pressure, the heat added is equal to the change in total heat of the gaseous mixture. The total heat Q of the gaseous mixture with water vapor and carbon dioxide dissociated to the fractions assumed, is obtained for any absolute temperature T by adding the internal energies of all gaseous constituents and the PV product of the whole gaseous mixture; thus:

$$\begin{aligned} Q = {} & (1\text{-}x)\ m\ U \text{ (for } H_2O) \\ & + xm\ U \text{ (for } H_2) \\ & + (1\text{-}y)\ k\ U \text{ (for } CO_2) \\ & + yk\ U \text{ (for CO)} \\ & + (o + xm/2 + yk/2)\ U \text{ (for } O_2) \\ & + n\ U \text{ (for } N_2) \\ & + (g + xm/2 + yk/2)\ ART \text{ (for gaseous mixture)} \end{aligned}$$

The several U's are the internal energies in Btu per lb-mole of the gaseous constituents indicated and $ART = 1.985\ T$ Btu per lb-mole is the PV-product per mole of gaseous mixture.

In the article entitled, "Thermal Properties of Gases" in COMBUSTION for July 1930, will be found an expression for the change in entropy dS of a gas, namely:

$$dS = C_v \frac{dT}{T} - AR\frac{dP}{P}$$
$$= (C_v + AR)\frac{dT}{T} - AR\frac{dP}{P}$$

Integrating,

$$S = \int_o^T C_v \frac{dT}{T} + AR \log_e T - AR \log_e P + S'_o$$

where S'_o is the constant of integration. In the first term, the specific heat at constant volume C_v is a function of T. For the gaseous mixture in question, we have:

$$\begin{aligned} S = {} & (1\text{-}x)\ m \left[\int_o^T C_v \frac{dT}{T} - AR \log_e P\right] \text{ (for } H_2O) \\ & + xm \left[\int_o^T C_v \frac{dT}{T} - AR \log_e P\right] \text{ (for } H_2) \\ & + (1\text{-}y)\ k \left[\int_o^T C_v \frac{dT}{T} - AR \log_e P\right] \text{ (for } CO_2) \\ & + yk \left[\int_o^T C_v \frac{dT}{T} - AR \log_e P\right] \text{ (for CO)} \\ & + (o + xm/2 + yk/2) \left[\int_o^T C_v \frac{dT}{T} - AR \log_e P\right] \text{ (for } O_2) \\ & + n \left[\int_o^T C_v \frac{dT}{T} - AR \log_e P\right] \text{ (for } N_2) \\ & + (g + xm/2 + yk/2)\ [AR \log_e T + S_o] \text{ (for gaseous mixture)} \end{aligned}$$

The several P's are the partial pressures in atmospheres of the gaseous constituents indicated. The several constants of integration have been combined into the one constant S_o.

Substituting in expressions (3) and (4), we obtain: For dissociation of water vapor,

$$\begin{aligned} \frac{dF}{dx} = {} & -m \left[U - T\int_o^T C_v \frac{dT}{T} + ART \log_e P\right] \text{ (for } H_2O) \\ & + m \left[U - T\int_o^T C_v \frac{dT}{T} + ART \log_e P\right] \text{ (for } H_2) \\ & + m/2 \left[U - T\int_o^T C_v \frac{dT}{T} + ART \log_e P\right] \text{ (for } O_2) \\ & + m/2\ [ART - ART \log_e T - T\,S_o] \text{ (for gaseous mixture)} \end{aligned}$$

For dissociation of carbon dioxide,

$$\begin{aligned} \frac{dF}{dy} = {} & -k \left[U - T\int_o^T C_v \frac{dT}{T} + ART \log_e P\right] \text{ (for } CO_2) \\ & + k \left[U - T\int_o^T C_v \frac{dT}{T} + ART \log_e P\right] \text{ (for CO)} \\ & + k/2 \left[U - T\int_o^T C_v \frac{dT}{T} + ART \log_e P\right] \text{ (for } O_2) \\ & + k/2 [ART - ART \log_e T - T\,S_o] \text{ (for gaseous mixture)} \end{aligned}$$

The chemical reaction of dissociation or association will proceed so long as the driving force dF/dx or dF/dy has a value other than zero. When $dF/dx = O$ and $dF/dy = O$, equilibrium has been reached. Equating the preceding expressions to zero and combining the terms involving the partial pressures of the gaseous constituents, we find:
For dissociation of water vapor at equilibrium,

$$ART \log_e \frac{P_{H_2O}}{P_{H_2}\sqrt{P_{O_2}}} = -U_{H_2O} + U_{H_2} + \tfrac{1}{2}\,U_{O_2}$$

$$+T\int_O^T (C_{H_2O} - C_{H_2} - {}^1/_2\, C_{O_2})\,\frac{dT}{T}$$
$$+{}^1/_2 T\,[AR - AR\log_e T - S_O]$$

For dissociation of carbon dioxide at equilibrium,

$$ART\log_e \frac{P_{CO_2}}{P_{CO}\sqrt{P_{O_2}}} = -U_{CO_2} + U_{CO} + {}^1/_2\, U_{O_2}$$
$$+T\int_O^T (C_{CO_2} - C_{CO} - {}^1/_2\, C_{O_2})\,\frac{dT}{T}$$
$$+{}^1/_2 T\,[AR - AR\log_e T - S_O]$$

Now, the internal energy of one mole of hydrogen (U_{H_2}) plus the internal energy of one-half mole of oxygen (${}^1/_2\, U_{O_2}$) which combines with the hydrogen minus the internal energy of the one mole of water vapor formed (U_{H_2O}), is equal to the energy given out by the combination, or the heating value per mole of hydrogen, at constant volume and at constant absolute temperature T. That is,

$$-U_{H_2O} + U_{H_2} + {}^1/_2\, U_{O_2} = H_{H_2}$$

For similar reasons,

$$-U_{CO_2} + U_{CO} + {}^1/_2 U_{O_2} = H_{CO}$$

where H_{CO} is the heating value per mole of carbon monoxide at constant volume and at constant absolute temperature T.

Heating values of fuels are usually determined experimentally at room temperature as explained in the article entitled, "Composition and Heating Value of Fuels," COMBUSTION, May 1931. The heating value at any other absolute temperature T differs from the heating value at room temperature but can be calculated therefrom if the specific heats are known of the several gaseous constituents existing before and after combustion. A simpler mathematical expression results, however, if the heating value H at absolute temperature T is related to a fictitious heating value $H°$ at absolute zero, the latter being calculated from the experimentally determined heating value at room temperature. The relations between H and $H°$ are:
For hydrogen,

$$H_{H_2} = H°_{H_2} + \int_O^T (C_{H_2} + {}^1/_2\, C_{O_2} - C_{H_2O})\,dT$$

For carbon monoxide,

$$H_{CO} = H°_{CO} + \int_O^T (C_{CO} + {}^1/_2\, C_{O_2} - C_{CO_2})\,dT$$

At absolute zero, the heating value at constant volume is equal to the heating value at constant pressure, so that $H°$ represents either quantity. By using specific heats at constant volume, the above expressions enable the constant volume heating value at absolute temperature T to be calculated when $H°$ is known. By using specific heats at constant pressure, the above expressions enable the constant pressure heating value at absolute temperature T to be calculated when $H°$ is known. These expressions may also be used to calculate $H°$ from experimental heating values at room temperature whether made at constant volume in a bomb calorimeter or at constant pressure in a flow-type calorimeter.

From chemical equation (1), it is evident that the heat produced by combustion of one mole of hydrogen H_{H_2} is equal to the heat required for dissociation of one mole of water vapor H_{H_2O}. It is likewise evident from chemical equation (2) that the heat produced by combustion of one mole of carbon monoxide H_{CO} is equal to the heat required for dissociation of one mole of carbon dioxide H_{CO_2}. The heats of dissociation will therefore be substituted for the heating values in the mathematical expressions for dissociation of water vapor and of carbon dioxide.

Substituting in the preceding mathematical expressions, we have:
For dissociation of water vapor,

$$ART\log_e \frac{P_{H_2O}}{P_{H_2}\sqrt{P_{O_2}}} = H°_{H_2O} - \int_O^T (C_{H_2O} - C_{H_2} - {}^1/_2 C_{O_2})\,dT$$
$$+T\int_O^T (C_{H_2O} - C_{H_2} - {}^1/_2\, C_{O_2})\,\frac{dT}{T}$$
$$+{}^1/_2 T\ \ [AR - AR\log_e T - S_O]$$

For dissociation of carbon dioxide,

$$ART\log_e \frac{P_{CO_2}}{P_{CO}\sqrt{P_{O_2}}} = H°_{CO_2} - \int_O^T (C_{CO_2} - C_{CO} - {}^1/_2 C_{O_2})\,dT$$
$$+T\int_O^T (C_{CO_2} - C_{CO} - {}^1/_2 C_{O_2})\,\frac{dT}{T}$$
$$+{}^1/_2 T\ \ [AR - AR\log_e T - S_O]$$

For any one of these gases, the specific heat at constant volume C is a function of the absolute temperature T and may be represented by

$$C = C_p - AR = a + bT + cT^2 - AR$$

Where C_p is the specific heat at constant pressure and a, b and c are constants.

Substituting in the preceding mathematical expressions, the above function of T for the specific heat at constant volume of each of the gaseous constituents, then integrating and dividing by T, we obtain:
For dissociation of water vapor,

$$AR\log_e \frac{P_{H_2O}}{P_{H_2}\sqrt{P_{O_2}}} = \frac{H°_{H_2O}}{T} - a\log_e T$$
$$- {}^1/_2\, bT^2 - {}^1/_6\, cT^3 - (S_o - a)$$
$$\text{where } a = a_{H_2} + {}^1/_2\, a_{O_2} - a_{H_2O}$$
$$b = b_{H_2} + {}^1/_2\, b_{O_2} - b_{H_2O}$$
$$c = c_{H_2} + {}^1/_2\, c_{O_2} - c_{H_2O}$$

For dissociation of carbon dioxide,

$$AR\log_e \frac{P_{CO_2}}{P_{CO}\sqrt{P_{O_2}}} = \frac{H°_{CO_2}}{T} - a\log_e T$$
$$- {}^1/_2\, bT^2 - {}^1/_6\, cT^3 - (S_o - a)$$
$$\text{where } a = a_{CO} + {}^1/_2\, a_{O_2} - a_{CO_2}$$
$$b = b_{CO} + {}^1/_2\, b_{O_2} - b_{CO_2}$$
$$c = c_{CO} + {}^1/_2\, c_{O_2} - c_{CO_2}$$

The values of a, b and c for the several gaseous constituents will be used as given in Table I. With the exception of hydrogen, these values are taken from University of Illinois Bulletin No. 139, entitled "An Investigation of the Maximum Temperatures and Pressures Attainable in the Combustion of Gaseous and Liquid Fuels" by Goodenough and Felbeck. Two simpler expressions below and above 2900 F absolute, respectively, are used for carbon dioxide instead of the more comprehensive expression given in the article entitled, "Thermal Properties of Gases" in COMBUSTION, July 1930. For hydrogen, values derived by R. F. Nielsen to fit data in the

International Critical Tables were tabulated instead of the values used by Goodenough and Felbeck because the latter are not in agreement with reliable specific heat data at room temperature.

TABLE I—CONSTANTS IN FORMULAS FOR SPECIFIC HEATS OF GASES AT CONSTANT PRESSURE

Gas	a	$b \times 10^3$	$c \times 10^6$
Water vapor, H_2O	8.33	−0.276	0.423
Carbon dioxide, CO_2			
Below 2900 F abs.	7.15	3.9	−0.6
Above 2900 F abs.	12.196	0.42	....
Carbon monoxide, CO, and Oxygen, O_2	6.93	....	0.12
Hydrogen, H_2	6.64	0.39	....

By means of these data for specific heats, the heats of dissociation of water vapor and of carbon dioxide "at absolute zero" have been calculated from the heating values of hydrogen and of carbon monoxide at room temperature, and found to be as follows:

For dissociation of water vapor,

$H^\circ_{H_2O}$ = 102530 Btu per lb-mole at absolute zero.

For dissociation of carbon dioxide,

$H^\circ_{CO_2}$ = 120930 Btu per lb-mole at absolute zero.

Substituting the data for the several gases, we obtain:
For dissociation of water vapor,

$$4.571 \log_{10} \frac{P_{H_2O}}{P_{H_2}\sqrt{P_{O_2}}} = \frac{102530}{T} - 4.0871 \log_{10} T - 0.333 \times 10^{-3} T + 0.0605 \times 10^{-6} T^2 + 2.5$$

For dissociation of carbon dioxide below 2900 F abs.,

$$4.571 \log_{10} \frac{P_{CO_2}}{P_{CO}\sqrt{P_{O_2}}} = \frac{120930}{T} - 7.4719 \log_{10} T + 1.95 \times 10^{-3} T - 0.13 \times 10^{-6} T^2 + 0.6$$

For dissociation of carbon dioxide above 2900 F abs.,

$$4.571 \log_{10} \frac{P_{CO_2}}{P_{CO}\sqrt{P_{O_2}}} = \frac{125810}{T} + 4.147 \log_{10} T + 0.21 \times 10^{-3} T - 0.03 \times 10^{-6} T^2 - 37.107$$

The values of the last constants in the above equations were determined by reference to experimental data. For dissociation of water vapor, Fig. 1 shows how the constant selected makes the curve fit the experimental points. For dissociation of carbon dioxide, Fig. 2 shows how the two constants selected make the curve fit the experimental points, the two constants being selected to give the same calculated value at the common temperature of 2900 F. Table II contains equilibrium constants for dissociation of water vapor and of carbon dioxide, calculated by the above equations to very high temperatures.
The values tabulated of

$$K_{H_2O} = \frac{P_{H_2O}}{P_{H_2} P_{O_2}^{0.5}} \quad (5) \quad \text{and} \quad K_{CO_2} = \frac{P_{CO_2}}{P_{CO} P_{O_2}^{0.5}} \quad (6)$$

are known as the equilibrium constants for dissociation of water vapor and of carbon dioxide, respectively. These two examples are representative of the more general relation that the equilibrium constant in any chemical reaction is equal to the product of the partial pressures of the reacting molecules divided by the product of the partial pressures of the molecules formed, each partial pressure being raised to a power equal to the number of molecules entering the reaction or being formed thereby. This so-called "law of mass action" was first formulated upon an experimental basis in 1867 by Guldberg and Waage and later established on thermodynamic grounds by van't Hoff and others.

When hydrogen or carbon monoxide is burned with just the right quantity of pure oxygen for complete combustion, there is a definite amount of each dissociated under equilibrium conditions at any particular temperature and total gas pressure. When atmospheric air instead of pure oxygen is supplied for combustion, the dissociation is different with the same total gas pressure. And when excess air is supplied for combustion, the fractions dissociated vary with the percentage of excess air. A method has been developed, however, for calculating the fractions of water vapor and of carbon dioxide dissociated under any conditions. This method will be explained and illustrated.

Thus, in expressions (5) and (6) for the equilibrium constants for dissociation of water vapor and of carbon dioxide, substitute the partial pressures of H_2O, H_2, CO_2 and CO in terms of the total gas pressure and the mole-fractions of these constituents. After cancellation of the same quantities in the numerator and the denominator, we obtain:
For dissociation of water vapor,

$$K_{H_2O} = \frac{1 - x}{\sqrt{x P_O}}$$

Whence, fraction of water vapor dissociated,

$$x = \frac{1}{1 + K_{H_2O}\sqrt{P_{O_2}}} \quad (7)$$

For dissociation of carbon dioxide,

$$K_{CO_2} = \frac{1 - y}{y\sqrt{P_{O_2}}}$$

Whence, fraction of carbon dioxide dissociated,

$$y = \frac{1}{1 + K_{CO_2}\sqrt{P_{O_2}}} \quad (8)$$

In the above formulas, P_{O_2} is the partial pressure in atmospheres of the oxygen in the gaseous mixture after dissociation has occurred and equilibrium has been established. But this partial pressure cannot be calculated until we know the fractions of water vapor and of carbon dioxide dissociated. We can, however, calculate the partial pressure of oxygen under the assumption of complete combustion without dissociation. The latter value can be used to calculate approximate values for the fracton x of water vapor dissociated and for the fraction y of carbon dioxide dissociated. The partial pressure of oxygen can then be recalculated for these approximate values of x and y. By use of the recalculated partial pressure of oxygen, more nearly correct values of x and y can be found. With very small excess air percentages, the calculations can be repeated if desirable to obtain a closer approach to the true values of x and y. With moderate and large excess air percentages, it is not necessary to recalculate x and y because the first approximate values are sufficiently accurate.

To simplify such calculations, Tables III and IV and the curves of Fig. 3 and Fig. 4 have been prepared to show the fractions of water vapor and of carbon dioxide

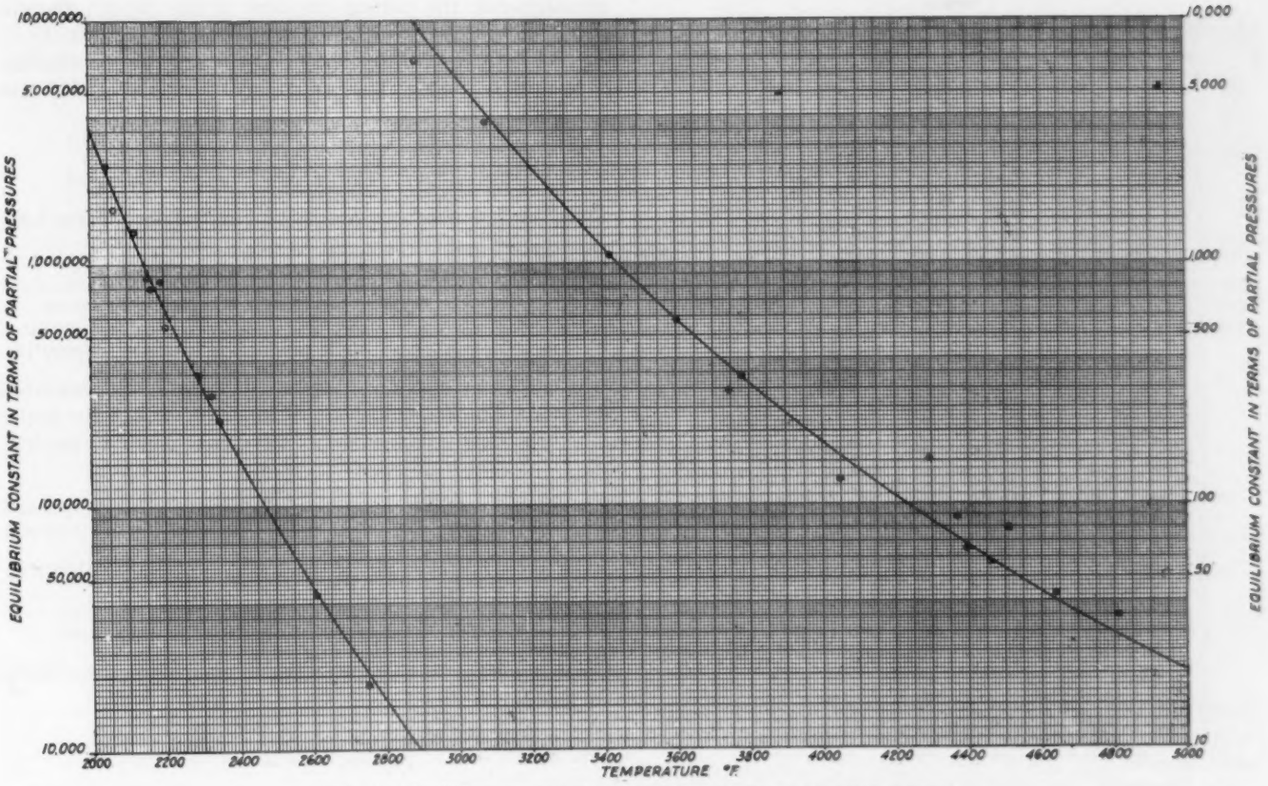

Fig. 1—Equilibrium constant for dissociation of water vapor

Comparison of theoretical curve with experimental data of Langmuir, Nernst, von Wartenburg, Lowenstein, Bjerrum and Siggel from International Critical Tables and University of Illinois Bulletin No. 139

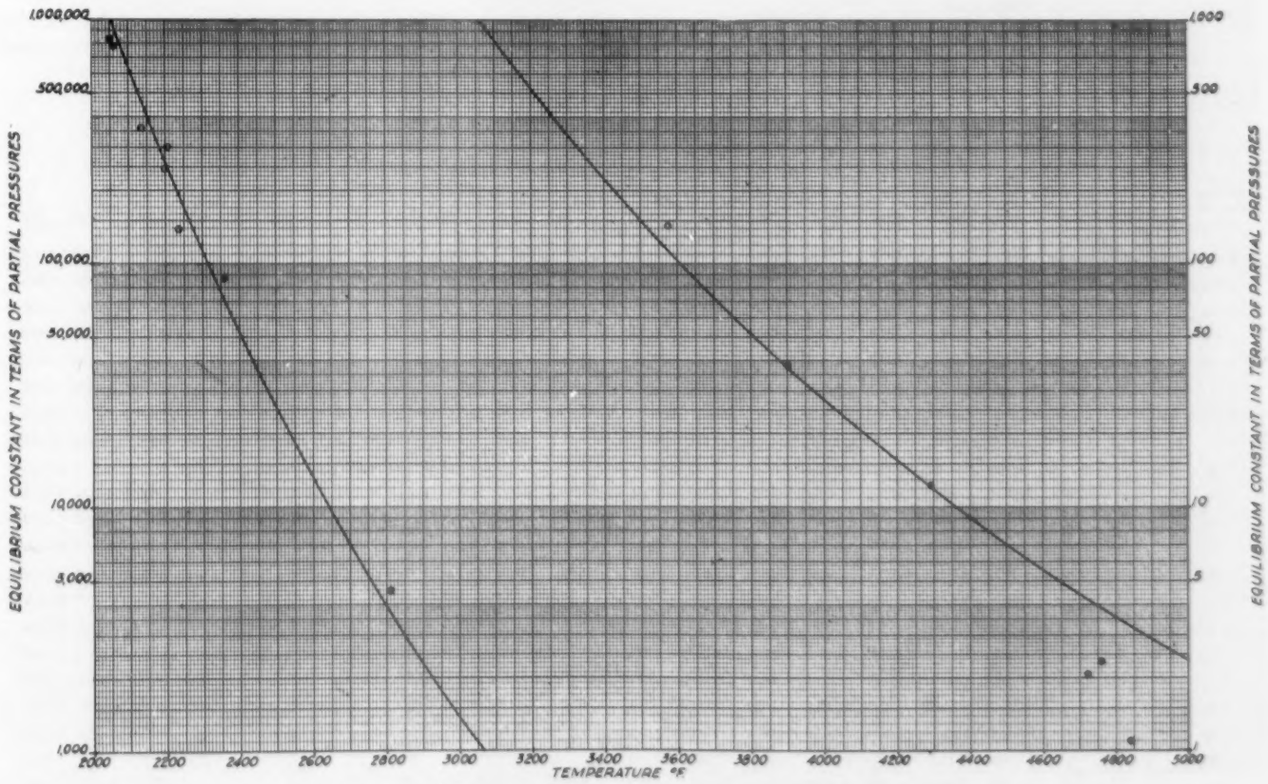

Fig. 2—Equilibrium constant for dissociation of carbon dioxide

Comparison of theoretical curve with experimental data of Langmuir, Nernst and von Wartenburg, Lowenstein, Emich and Bjerrum from University of Illinois Bulletin No. 139

TABLE II

EQUILIBRIUM CONSTANTS FOR DISSOCIATION OF WATER VAPOR AND OF CARBON DIOXIDE IN TERMS OF PARTIAL PRESSURES

Temp., Fahr.	K_{H_2O}	K_{CO_2}	Temp., Fahr.	K_{H_2O}	K_{CO_2}
2000	5432000	1668000	4000	178.7	27.49
2100	1455000	633300	4100	137.4	20.47
2200	658000	259100	4200	106.8	15.45
2300	315000	113300	4300	84.05	11.78
2400	158700	52530	4400	66.80	9.096
2500	83630	25660	4500	53.63	7.093
2600	45970	13160	4600	43.49	5.586
2700	26240	7042	4700	35.59	4.437
2800	15500	3920	4800	29.36	3.557
2900	9447	2259	4900	24.40	2.874
3000	5922	1346	5000	20.45	2.340
3100	3815	825.8	5100	17.26	1.919
3200	2515	520.4	5200	14.66	1.584
3300	1697	336.2	5300	12.55	1.317
3400	1168	222.2	5400	10.80	1.100
3500	820.4	150.0	5500	9.352	0.9249
3600	586.3	103.3	5600	8.146	0.7821
3700	426.2	72.44	5700	7.139	0.6646
3800	314.4	51.67	5800	6.288	0.5677
3900	235.3	37.41	5900	5.561	0.4871
4000	178.7	27.49	6000	4.942	0.4194

dissociated in products of combustion at temperatures up to 400 F and with oxygen partial pressures up to one atmosphere.

To illustrate the use of these tabulated values and curves, assume that for complete combustion of a typical Pittsburgh bituminous coal with 30 per cent excess air, we have in one mole of the moist products of combustion:

0.07067 mole H_2O
0.13261 mole CO_2
0.04598 mole O_2
0.75074 mole N_2

1.00000 mole moist products

If the total pressure of the moist gaseous mixture is 1.1 atmospheres, the partial pressure of the oxygen therein is $1.1 \times 0.04598 = 0.05058$ atmosphere. At 3500 F, we find by using formulas (5) and (6) and the equilibrium constants in Table II, or by referring to Tables III and IV or the curves of Fig. 3 and Fig. 4:

$x = 0.0054$ or 0.54 per cent of water vapor dissociated.
$y = 0.0288$ or 2.88 per cent of carbon dioxide dissociated.

These are the first approximations to the actual fractions dissociated and correspond to

$0.07067 \times 0.0054 = 0.00038$ mole of water vapor dissociated per mole of products of complete combustion.
$0.13261 \times 0.0288 = 0.00382$ mole of carbon dioxide dissociated per mole of products of complete combustion.

If the water vapor and carbon dioxide were dissociated to these amounts, the moles of free oxygen and the moles of moist products would both be increased by one-half the sum of these amounts, so that we would have:

$0.04598 + 0.00019 + 0.00191 = 0.04808$ mole of free oxygen and
$1.00000 + 0.00019 + 0.00191 = 1.00210$ moles of moist products.

The partial pressure of the free oxygen after dissociation would therefore be:

$$1.1 \times 0.0.04808/1.00210 = 0.05278 \text{ atmosphere.}$$

Corresponding to this corrected oxygen partial pressure, we find:

$x = 0.0053$ or 0.53 per cent of water vapor dissociated
$y = 0.0282$ or 2.82 per cent of carbon dioxide dissociated.

The recalculated fractions are so close to the first approximations that additional recalculations are unnecessary. In fact, the first approximations are sufficiently close to the true values for most purposes.

The chemical reactions of dissociation of water vapor and carbon dioxide are together equivalent to the "water-gas reaction," so-called because it is important in the production of fuel gas from steam and incandescent carbon, namely:

$$H_2O + CO = H_2 + CO_2$$

TABLE III

FRACTION OF WATER VAPOR DISSOCIATED IN PRODUCTS OF COMBUSTION

Oxygen partial pressure, atm.	Temperature, Fahr.																				
	2000	2100	2200	2300	2400	2500	2600	2700	2800	2900	3000	3100	3200	3300	3400	3500	3600	3700	3800	3900	4000
0.002	0.00001	0.00001	0.00003	0.00007	0.00014	0.00027	0.00049	0.00085	0.00144	0.00236	0.0038	0.0058	0.0086	0.0130	0.0188	0.0265	0.0367	0.0498	0.0664	0.0868	0.1112
0.004	0.00000	0.00001	0.00002	0.00005	0.00010	0.00019	0.00034	0.00060	0.00102	0.00167	0.0027	0.0041	0.0062	0.0092	0.0134	0.0189	0.0263	0.0358	0.0479	0.0630	0.0813
0.006		0.00001	0.00002	0.00004	0.00008	0.00015	0.00028	0.00049	0.00083	0.00136	0.0022	0.0034	0.0051	0.0075	0.0109	0.0155	0.0216	0.0294	0.0394	0.0520	0.0674
0.008		0.00001	0.00002	0.00004	0.00007	0.00013	0.00024	0.00043	0.00072	0.00118	0.0019	0.0029	0.0044	0.0065	0.0095	0.0134	0.0187	0.0256	0.0343	0.0454	0.0589
0.010		0.00001	0.00002	0.00003	0.00006	0.00012	0.00022	0.00038	0.00064	0.00106	0.0017	0.0026	0.0040	0.0059	0.0085	0.0120	0.0168	0.0229	0.0308	0.0408	0.0530
0.02		0.00000	0.00001	0.00002	0.00004	0.00008	0.00015	0.00027	0.00046	0.00075	0.0012	0.0019	0.0028	0.0041	0.0060	0.0085	0.0119	0.0163	0.0220	0.0292	0.0381
0.03			0.00001	0.00002	0.00004	0.00007	0.00013	0.00022	0.00037	0.00061	0.0010	0.0015	0.0023	0.0034	0.0049	0.0070	0.0098	0.0134	0.0180	0.0239	0.0313
0.04			0.00001	0.00002	0.00003	0.00006	0.00011	0.00019	0.00032	0.00053	0.0008	0.0013	0.0020	0.0029	0.0043	0.0061	0.0085	0.0116	0.0157	0.0208	0.0272
0.05			0.00001	0.00001	0.00003	0.00005	0.00010	0.00017	0.00029	0.00047	0.0008	0.0012	0.0018	0.0026	0.0038	0.0054	0.0076	0.0104	0.0140	0.0186	0.0244
0.06			0.00001	0.00001	0.00003	0.00005	0.00009	0.00016	0.00026	0.00043	0.0007	0.0011	0.0016	0.0024	0.0035	0.0050	0.0069	0.0095	0.0128	0.0171	0.0223
0.07			0.00001	0.00001	0.00002	0.00005	0.00008	0.00014	0.00024	0.00040	0.0006	0.0010	0.0015	0.0022	0.0032	0.0046	0.0064	0.0088	0.0119	0.0158	0.0207
0.08			0.00001	0.00001	0.00002	0.00004	0.00008	0.00013	0.00023	0.00037	0.0006	0.0009	0.0014	0.0021	0.0030	0.0043	0.0060	0.0082	0.0111	0.0148	0.0194
0.09			0.00001	0.00001	0.00002	0.00004	0.00007	0.00013	0.00022	0.00035	0.0006	0.0009	0.0013	0.0020	0.0028	0.0040	0.0057	0.0078	0.0105	0.0140	0.0183
0.10			0.00000	0.00001	0.00002	0.00004	0.00007	0.00012	0.00020	0.00033	0.0005	0.0008	0.0013	0.0019	0.0027	0.0038	0.0054	0.0074	0.0100	0.0133	0.0174
0.12				0.00001	0.00002	0.00003	0.00006	0.00011	0.00019	0.00031	0.0005	0.0008	0.0011	0.0017	0.0025	0.0035	0.0049	0.0067	0.0091	0.0121	0.0159
0.14				0.00001	0.00002	0.00003	0.00006	0.00010	0.00017	0.00028	0.0005	0.0007	0.0011	0.0016	0.0023	0.0032	0.0045	0.0062	0.0084	0.0112	0.0147
0.16				0.00001	0.00002	0.00003	0.00005	0.00010	0.00016	0.00026	0.0004	0.0007	0.0010	0.0015	0.0021	0.0030	0.0042	0.0058	0.0079	0.0105	0.0138
0.18				0.00001	0.00001	0.00003	0.00005	0.00009	0.00015	0.00025	0.0004	0.0006	0.0009	0.0014	0.0020	0.0029	0.0040	0.0055	0.0074	0.0099	0.0130
0.20				0.00001	0.00001	0.00003	0.00005	0.00009	0.00014	0.00024	0.0004	0.0006	0.0009	0.0013	0.0019	0.0027	0.0038	0.0052	0.0071	0.0094	0.0124
0.30				0.00001	0.00001	0.00002	0.00004	0.00007	0.00012	0.00019	0.0003	0.0005	0.0007	0.0011	0.0016	0.0022	0.0031	0.0043	0.0058	0.0077	0.0101
0.40				0.00001	0.00001	0.00002	0.00003	0.00006	0.00010	0.00017	0.0003	0.0004	0.0006	0.0009	0.0014	0.0019	0.0027	0.0037	0.0050	0.0067	0.0088
0.50				0.00000	0.00001	0.00002	0.00003	0.00005	0.00009	0.00015	0.0002	0.0004	0.0006	0.0008	0.0012	0.0017	0.0024	0.0033	0.0045	0.0060	0.0079
1.00					0.00001	0.00001	0.00002	0.00004	0.00006	0.00011	0.0002	0.0003	0.0004	0.0006	0.0009	0.0012	0.0017	0.0023	0.0032	0.0042	0.0056

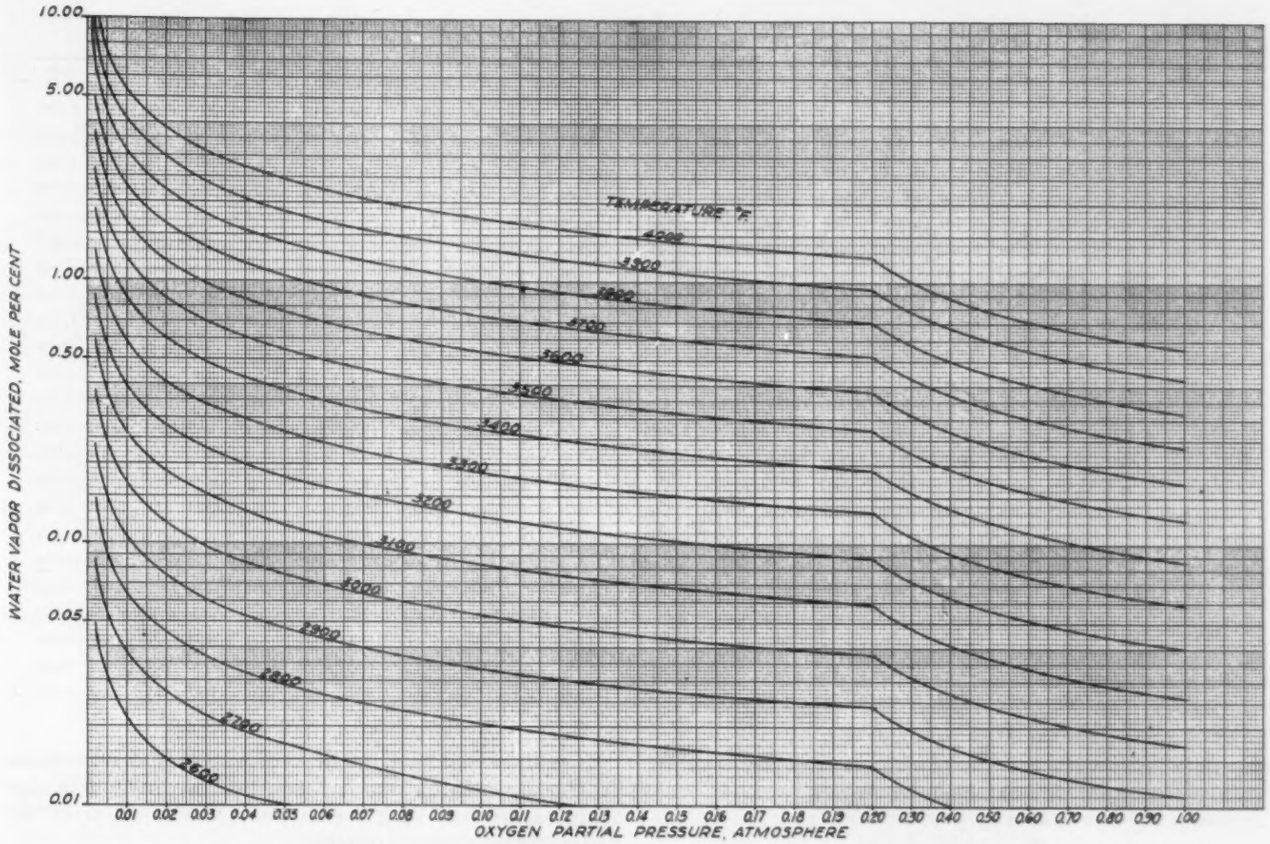

Fig. 3—Water vapor dissociated in products of combustion at equilibrium

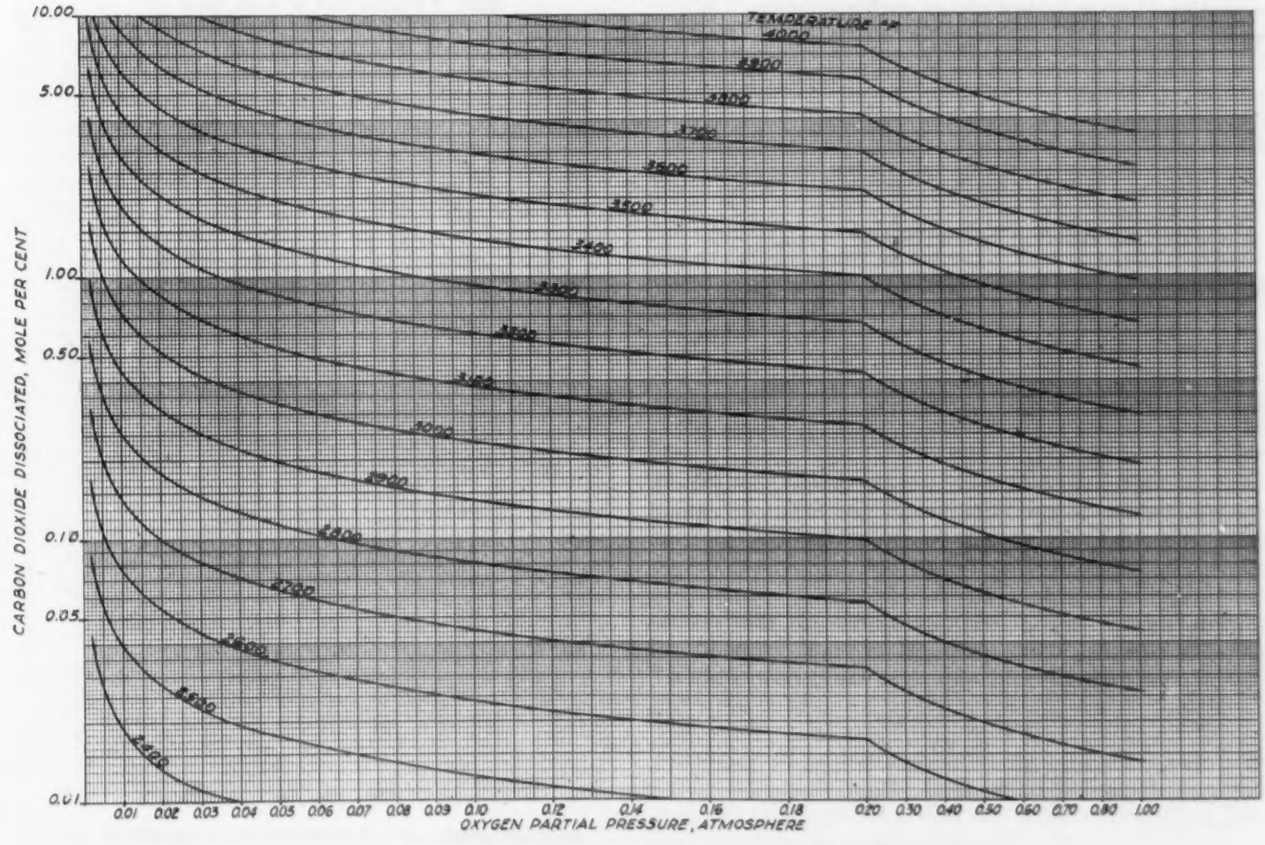

Fig. 4—Carbon dioxide dissociated in products of combustion

TABLE IV

FRACTION OF CARBON DIOXIDE DISSOCIATED IN PRODUCTS OF COMBUSTION

Oxygen partial pressure, atm.	2000	2100	2200	2300	2400	2500	2600	2700	2800	2900	3000	3100	3200	3300	3400	3500	3600	3700	3800	3900	4000
0.002	0.00001	0.00004	0.00009	0.00020	0.00043	0.00087	0.00170	0.00317	0.00567	0.00980	0.0163	0.0264	0.0412	0.0621	0.0911	0.1297	0.1779	0.2359	0.3021	0.3741	0.4486
0.004	0.00001	0.00002	0.00006	0.00014	0.00030	0.00062	0.00120	0.00224	0.00402	0.00695	0.0116	0.0188	0.0295	0.0449	0.0664	0.0954	0.1327	0.1792	0.2343	0.2971	0.3652
0.006	0.00001	0.00002	0.00005	0.00011	0.00025	0.00050	0.00098	0.00183	0.00328	0.00568	0.0095	0.0154	0.0242	0.0370	0.0549	0.0792	0.1111	0.1513	0.1999	0.2565	0.3196
0.008	0.00001	0.00002	0.00004	0.00010	0.00021	0.00044	0.00085	0.00159	0.00284	0.00492	0.0082	0.0134	0.0210	0.0322	0.0479	0.0694	0.0976	0.1337	0.1779	0.2301	0.2892
0.010	0.00001	0.00002	0.00004	0.00009	0.00019	0.00039	0.00076	0.00142	0.00254	0.00441	0.0074	0.0120	0.0189	0.0289	0.0431	0.0625	0.0882	0.1213	0.1622	0.2109	0.2668
0.02	0.00000	0.00001	0.00003	0.00006	0.00013	0.00028	0.00054	0.00100	0.00180	0.00312	0.0052	0.0085	0.0134	0.0206	0.0308	0.0450	0.0641	0.0889	0.1204	0.1590	0.2046
0.03		0.00001	0.00002	0.00005	0.00011	0.00022	0.00044	0.00082	0.00147	0.00255	0.0043	0.0069	0.0110	0.0169	0.0253	0.0371	0.0529	0.0738	0.1005	0.1337	0.1736
0.04		0.00001	0.00002	0.00004	0.00010	0.00019	0.00038	0.00071	0.00127	0.00221	0.0037	0.0060	0.0095	0.0147	0.0220	0.0323	0.0462	0.0646	0.0882	0.1179	0.1539
0.05		0.00001	0.00002	0.00004	0.00009	0.00017	0.00034	0.00063	0.00114	0.00198	0.0033	0.0054	0.0085	0.0131	0.0197	0.0289	0.0415	0.0581	0.0797	0.1068	0.1399
0.06		0.00001	0.00002	0.00004	0.00008	0.00016	0.00031	0.00058	0.00104	0.00180	0.0030	0.0049	0.0078	0.0120	0.0180	0.0265	0.0380	0.0533	0.0732	0.0984	0.1293
0.07		0.00001	0.00001	0.00003	0.00007	0.00015	0.00029	0.00054	0.00096	0.00167	0.0028	0.0046	0.0072	0.0111	0.0167	0.0246	0.0353	0.0496	0.0682	0.0918	0.1209
0.08		0.00001	0.00001	0.00003	0.00007	0.00014	0.00027	0.00050	0.00090	0.00156	0.0026	0.0043	0.0067	0.0104	0.0157	0.0230	0.0331	0.0465	0.0640	0.0863	0.1140
0.09		0.00001	0.00001	0.00003	0.00006	0.00013	0.00025	0.00047	0.00085	0.00147	0.0025	0.0040	0.0064	0.0098	0.0148	0.0217	0.0313	0.0440	0.0606	0.0818	0.1082
0.10		0.00000	0.00001	0.00003	0.00006	0.00012	0.00024	0.00045	0.00081	0.00140	0.0023	0.0038	0.0060	0.0093	0.0140	0.0206	0.0297	0.0418	0.0577	0.0779	0.1032
0.12			0.00001	0.00003	0.00005	0.00011	0.00022	0.00041	0.00074	0.00128	0.0021	0.0035	0.0055	0.0085	0.0128	0.0189	0.0272	0.0383	0.0529	0.0716	0.0950
0.14			0.00001	0.00002	0.00005	0.00010	0.00020	0.00038	0.00068	0.00118	0.0020	0.0032	0.0051	0.0079	0.0119	0.0175	0.0252	0.0356	0.0492	0.0667	0.0886
0.16			0.00001	0.00002	0.00005	0.00010	0.00019	0.00035	0.00064	0.00111	0.0019	0.0030	0.0048	0.0074	0.0111	0.0164	0.0236	0.0334	0.0462	0.0626	0.0834
0.18			0.00001	0.00002	0.00004	0.00009	0.00018	0.00033	0.00060	0.00104	0.0017	0.0028	0.0045	0.0070	0.0105	0.0155	0.0223	0.0315	0.0436	0.0593	0.0790
0.20			0.00001	0.00002	0.00004	0.00009	0.00017	0.00032	0.00057	0.00099	0.0017	0.0027	0.0043	0.0066	0.0100	0.0147	0.0212	0.0299	0.0415	0.0564	0.0752
0.30			0.00001	0.00002	0.00003	0.00007	0.00014	0.00026	0.00047	0.00081	0.0014	0.0022	0.0035	0.0054	0.0081	0.0120	0.0174	0.0246	0.0341	0.0465	0.0623
0.40			0.00001	0.00001	0.00003	0.00006	0.00012	0.00022	0.00040	0.00070	0.0012	0.0019	0.0030	0.0047	0.0071	0.0104	0.0151	0.0214	0.0297	0.0405	0.0544
0.50			0.00001	0.00001	0.00003	0.00006	0.00011	0.00020	0.00036	0.00063	0.0010	0.0017	0.0027	0.0042	0.0063	0.0093	0.0135	0.0191	0.0266	0.0364	0.0489
1.00			0.00000	0.00001	0.00002	0.00004	0.00008	0.00014	0.00026	0.00044	0.0007	0.0012	0.0019	0.0030	0.0045	0.0066	0.0096	0.0136	0.0190	0.0260	0.0352

In accordance with the law of mass action, the equilibrium constant for this water-gas reaction is:

$$K_{WG} = \frac{P_{H_2O} \times P_{CO}}{P_{H_2} \times P_{CO_2}}$$

By comparison with the equilibrium constants for dissociation of water vapor and of carbon dioxide, it is evident that

$$K_{WG} = \frac{K_{H_2O}}{K_{CO_2}}$$

Or, $$\log_{10} K_{WG} = \log_{10} K_{H_2O} - \log_{10} K_{CO_2}$$

Substituting the mathematical expressions for the latter terms, we find:

For water-gas reaction below 2900 F abs.,

$$4.571 \log_{10} K_{WG} = -\frac{18400}{T} + 3.3848 \log_{10} T - 2.283 \times 10^{-3} T + 0.1905 \times 10^{-6} T^2 + 1.9$$

For water-gas reaction below 2900 F abs.,

$$4.571 \log_{10} K_{WG} = -\frac{23280}{T} - 8.2341 \log_{10} T - 0.543 \times 10^{-3} T + 0.0905 \times 10^{-6} T^2 + 39.607$$

For the water-gas reaction, Fig. 5 shows how experimental values of the equilibrium constant correspond with the curve for the above equations derived from mathematical expressions for dissociation of water vapor and of carbon dioxide.

Substituting the partial pressures of the several gaseous constituents of products of combustion in the law of mass action for the water-gas reaction, we obtain:

$$K_{WG} = \frac{(1 - x)y}{x(1 - y)}$$

Whence, $$x/y = \frac{1}{y + (1 - y)K_{WG}}$$

$$= \frac{(1 - x) + K_{WG}}{K_{WG}}$$

It is thus seen that the ratio of water vapor to carbon dioxide dissociated is not a constant at any particular temperature but varies with the dissociation of either water vapor or carbon dioxide.

TABLE V

HEATS OF DISSOCIATION OF WATER VAPOR AND CARBON DIOXIDE IN BTU PER LB MOLE

Temp., Fahr.	H_2O	H_{CO_2}
2000	107,110	121,160
2100	107,230	121,000
2200	107,330	120,840
2300	107,420	120,680
2400	107,500	120,530
2500	107,560	120,380
2600	107,610	120,240
2700	107,650	120,100
2800	107,660	119,970
2900	107,660	119,850
3000	107,650	119,740
3100	107,610	119,640
3200	107,560	119,540
3300	107,480	119,460
3400	107,380	119,390
3500	107,270	119,320
3600	107,130	119,270
3700	106,970	119,230
3800	106,780	119,210
3900	106,570	119,190
4000	106,340	119,190

TABLE VI

SENSIBLE HEAT AND HEAT OF DISSOCIATION OF PRODUCTS OF COMBUSTION OF PITTSBURGH BITUMINOUS COAL BURNED WITH 30 PER CENT EXCESS AIR

Temp., Fahr.	Sensible heat in products of combustion per lb. of coal, B.t.u.	Heat of dissociation of H_2O and CO_2 per lb. of coal, B.t.u.	Sensible heat plus latent heat in products per lb. of coal, B.t.u.
2000	7420	--	7420
2100	7824	--	7824
2200	8231	0.2	8231
2300	8641	0.3	8641
2400	9050	0.8	9057
2500	9473	1.5	9475
2600	9895	2.9	9898
2700	10320	5.4	10325
2800	10749	9.5	10759
2900	11182	16.3	11198
3000	11620	27.2	11647
3100	12061	44.1	12105
3200	12507	69.3	12576
3300	12957	106.5	13064
3400	13412	159.5	13572
3500	13871	233.3	14104
3600	14335	333.7	14669
3700	14804	466.2	15270
3800	15278	638.0	15916
3900	15757	854.4	16611
4000	16242	1119.7	17362

The effect of dissociation of water vapor and of carbon dioxide in products of combustion is to reduce the heat that would otherwise be produced by combustion. This heat, however, is not lost, but exists as latent heat in the products of combustion. When the products of combustion are cooled, this latent heat is gradually given out as dissociation becomes less, thereby augmenting the heat given out by reduction in sensible heat of the products of combustion. It is therefore preferable, not to consider the heating value of the fuel as reduced by the heat of dissociation of the products of combustion, but to add the latter quantity to the sensible heat of the products of combustion.

The heats of dissociation per mole of water vapor and per mole of carbon dioxide are given in Table V. At 3500 F, the heat rendered latent by dissociation per mole of products of complete combustion of the Pittsburgh bituminous coal previously mentioned as burned with 30 per cent excess air, would be

$107{,}270 \times 0.00038 = 40.8$ Btu for dissociation of water vapor

$119{,}320 \times 0.00382 = 455.8$ Btu for dissociation of carbon dioxide.

As there were 0.4698 lb-moles of moist products of complete combustion per pound of coal burned, the heat of dissociation per pound of coal burned is:

$$(40.8 + 455.8) \times 0.4698 = 233.3 \text{ Btu}$$

This should be added to the sensible heat of the products of combustion rather than subtracted from the heating value of the coal. It represents, however, about 1.7 per cent of the heating value of the coal of 13,500 Btu per lb.

By similar calculations, the dissociation of the products of combustion and the heat rendered latent thereby have been calculated at temperatures from 2000 to 4000 F for this same Pittsburgh bituminous coal burned with 30 per cent excess air, and the results are tabulated in Table VI. It is seen that below 3000 F, the effects of dissociation are negligible but that above this temperature the heat rendered latent becomes appreciable with the products of combustion at 1.1. atmospheres pressure.

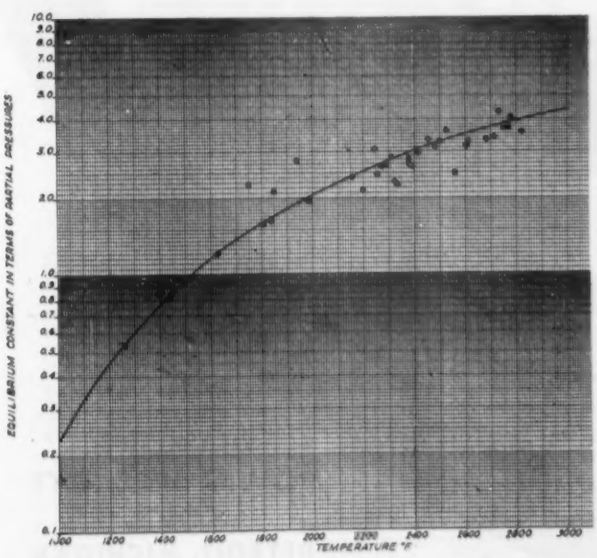

Fig. 5—Equilibrium constant for water-gas reaction

Comparison of theoretical curve with experimental data of Hahn, Harries, Allner, and Haber and Richardt from University of Illinois Bulletin No. 139

Summary and Conclusions

The preceding discussion shows that if appreciable proportions of carbon monoxide and of hydrogen exist in products of combustion below 3000 F, it is by reason of imperfections in the combustion process rather than by reaching equilibrium conditions in dissociation of carbon dioxide and water vapor in the products of combustion unless the air supplied for combustion closely approaches or is less than that theoretically required for complete combustion. This conclusion would only be changed by the unusual condition of combustion in a high vacuum where the partial pressure of the free oxygen in the products of combustion would be low.

Above 3000 F, dissociation becomes appreciable with combustion at atmospheric pressure. In certain metallurgical processes, therefore, it may be necessary to consider dissociation of water vapor and of carbon dioxide, but other data on equilibria might be necessary by reason of the presence of incandescent carbon rather than free oxygen. That is, the problem might be one concerning the combustion process rather than dissociation in products of combustion.

In steam boiler furnaces, the temperature seldom exceeds 3000 F, particularly in modern furnaces with water-cooled walls and ample volume. In steam boiler furnaces, therefore, it is in general unnecessary to consider dissociation of water vapor and carbon dioxide in the products of combustion. The presence of carbon monoxide in appreciable amounts in stack gases from steam boilers is rightly ascribed to incomplete combustion of carbon in the article on "Combustion Heat Balance" in COMBUSTION for June 1931.

A later article will deal with the combustion process.

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Investigate Turbine Losses with Compressed Air

A reprint from *Schiveizeriche Bauzeitung* of December 1934 relates some investigations by Messrs. Ackeret, Keller and Salzmann on large scale models of steam turbines using compressed air to determine what is going on in the various passages. The purpose in using air is to avoid the difficulties incident to experimenting with high-temperature steam and to the complications resulting from condensation in the passages.

It was found entirely practicable to study the high- and intermediate-pressure stages by this method, particularly leakage and short-circuits of the working fluid and the exit angle of the blades, although the processes in the low-pressure stages are not fully comparable as between steam and air. In order to establish the relation between these media the authors resort to a mathematical analysis which concludes that one fluid may be substituted for the other with precision if both have equal Reynolds and Mach coefficients.

New Type of Electric Boiler

An electric boiler which differs materially from all previous designs, both in its construction and its principle of operation, has been developed by Brown, Boveri & Company, Baden, Switzerland. In this boiler the electric current does not, as in the usual type, flow from immersed electrodes through a stationary column of water, but is conducted through water jets which radiate continuously from nozzles to the electrodes.

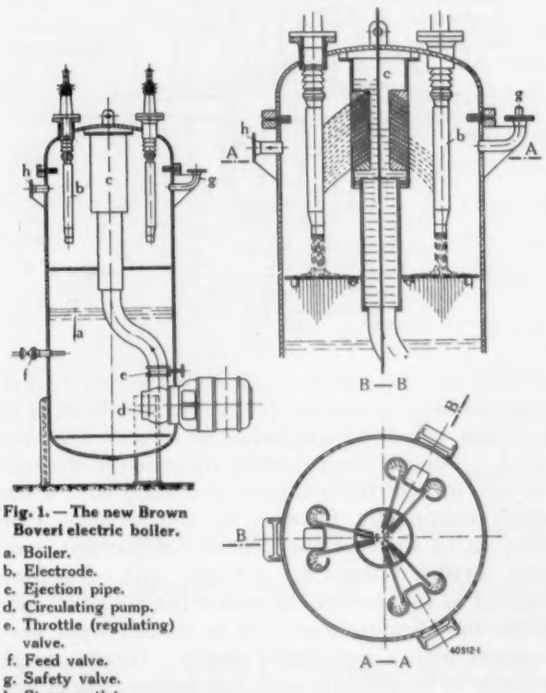


Fig. 1.—The new Brown Boveri electric boiler.

a. Boiler.
b. Electrode.
c. Ejection pipe.
d. Circulating pump.
e. Throttle (regulating) valve.
f. Feed valve.
g. Safety valve.
h. Steam outlet.

Sections through electric boiler

The three electrodes are arranged concentrically about the vertical ejection pipe, which is provided with three vertical double rows of nozzles. The circulating pump delivers water from the lower part of the boiler into this tube, from which it flows in jets against the electrodes. These are so constructed that the water impinges on their inner surfaces tangentially, spreads over the inner surface and is so deflected that it acquires a circulative and downward motion. The centrifugal effect assists the separation of the steam from the water. At their lower ends the spiral shape of the electrodes changes into a circular one so that a tubular extension is formed which collects the water caught in the spirals and concentrates it into a jet. Leaving the electrode at the bottom the water impinges on a perforated plate which is electrically connected with the walls of the boiler and flows into the collecting chamber.

The output of the boiler is regulated by varying the quantity of circulating water; that is, according to the output a smaller or greater number of nozzles will be in use. The boiler is built for inputs ranging from 300 to 10,000 kw.

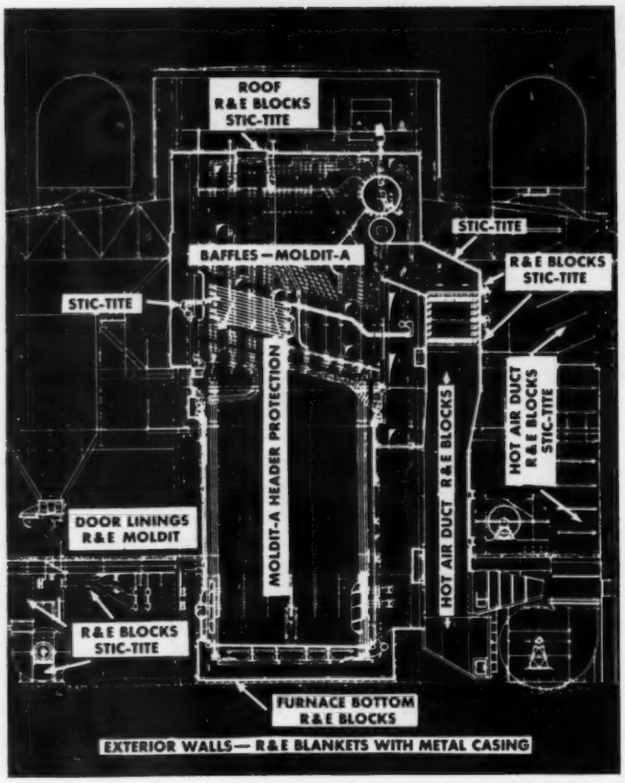
Uses Gravel to Blast Slag Deposits

Die Wärme for February describes the method employed in a German power station for removing slag from the boiler heating surface directly exposed to the furnace. This consists of a blast of fine gravel, about $^1/_8$ in. in size, which is directed against the slugged surfaces by an air blast under about 50 lb per sq in., more or less, depending upon conditions. A portable blast outfit is employed and the cost is said to be low. The gravel blast does not take the place of steam jets for blowing other locations in the boiler, but is very effective where the slag deposits are heavy and where temperature makes it difficult to use steam nozzles close to the deposits.

Unusual Air Heater Arrangement

An interesting feature of the New Swansea Power Station in England, which is scheduled to go into service this month and which is described in the April issue of *Engineering and Boiler House Review*, is the arrangement of the air heater. This is of the plate type and the heating surface is split into two sections—44 per cent being placed before the economizer and the remainder between the economizer and the induced-draft fan.

This scheme was adopted in order to secure an air



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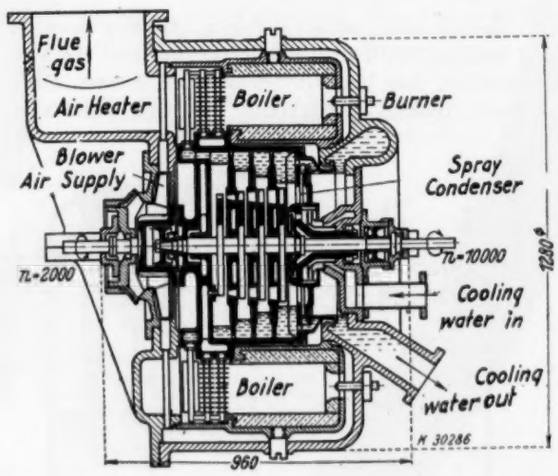
temperature of about 700 F to insure successful combustion with pulverized anthracite duff. While a high air temperature could have been obtained by placing the entire air heater ahead of the economizer, this would have penalized the latter.

The amount of air passing through an air heater is always considerably less than the weight of flue gas, hence the rise in air temperature exceeds the fall in gas temperature and with a large gas drop the air temperature in passing through the heater soon tends to approach the gas temperature. In this case considerable economy of air heater surface was obtained by interposing the economizer between the two sections of the heater and a reasonable temperature difference was obtained throughout the heater without sacrificing thermal efficiency.

Comments on the Hüttner Turbine

The Hüttner boiler-turbine unit, which has been proposed in Germany, employs the principle of the Vorkauf revolving boiler, and the boiler and turbine structures revolve in opposite directions. The illustration represents a cross-section of a 100-kw unit designed to revolve at 2000 rpm. Because of the peculiar construction of the Hüttner turbine, the condensate flows back into the boiler itself and consequently no condensate pump is required.

Commenting upon this design in a recent pamphlet Dr. Friedrich Münzinger, the well-known German engineer, observes that only experience will show whether the power consumption for revolving the boiler will not become too costly because of the windage losses and



whether the unit can be made to run quietly. Furthermore, he says, it will not be easy to so construct a large unit that it will remain balanced at such high rotative speed. Also, the unit is made up of many welded parts exposed to high temperatures and filled with a medium which continually changes in consistency. Opinions differ as to whether the delivery of feedwater will require auxiliary power for a larger unit. The question remains as to whether the power consumption involved in the unit feeding itself will be smaller than would be required with a centrifugal pump. Finally, regulation is likely to be difficult since the turbine works continuously with full open entrance nozzle area.

Cinder and Fly-Ash Measurements

Answer to Arthur C. Stern's Discussion in the April Issue

By P. H. HARDIE

Mr. Stern in the April issue, page 37, gives an interesting discussion of the author's article in the March issue of COMBUSTION and of dust sampling in general. He is apparently a strong believer in the adequacy of a single sampler spotted at a point in the duct where an average dust loading exists. The author has been unable to find a sampling location where the point of average dust loading did not change with at least several of the following: load, stoker fuel bed condition, damper position, relative speed of the two induced-draft fans, the unevenness of fouling on the gas side of the air preheater or economizer, and other operational factors. The author, however, agrees with Mr. Stern that for routine steam-generating unit efficiency tests and for frequent checks for the proper setting of burners and for regulation of stokers, a single sampler with a large size tube and cyclone separator is adequate.

The enthusiasm of Mr. Stern for his proposed method has led him to make certain critical statements of the procedure given in the article which the author feels called upon to refute.

Mr. Stern says that the dust loading appears to have been determined without weighting according to the respective velocities, yet when he computed the weighted average he got the same answer, which he calls "a most curious coincidence." As a matter of fact the two methods will always give the same answer. This will be evident when one stops to consider that the composite sample is already weighted when the quantity of dust-laden gas drawn from each point is proportional to the respective duct velocities. Mr. Stern merely used a round-about method of computing what had already been accomplished by the sampling procedure.

The point raised that a serious error is introduced by the procedure of shutting off the flow when necessary to correct trouble, can be answered by the statement that this possibility was investigated before adopting such a procedure. The straight vertical section and long radius bend of the sampling tube, shown in Figs. 2 and 3 of the original article, prevent any appreciable amount of cinders from being projected into the horizontal section, there to remain until carried over into the jar. This was determined by leaving the samplers shut off for half an hour, then turning on suddenly, and observing the rate at which the cinders were drawn into the jars. No shot of cinders could be detected when the flow was resumed. The average outage time to correct trouble is only about two minutes so the error could hardly be serious.

Concerning the loss of small size particles when emptying the bags, it has been found that this loss can easily be kept within 0.1 or 0.2 per cent. While there is no loss from emptying the catch when cyclone separators are used, Mr. Stern seems to overlook the fact that there is a loss before removing because no cyclone separator is 100 per cent efficient. In this connection, it is hard to attach any significance to the 30 per cent through 325 mesh screens which Mr. Stern says he was accustomed to obtain, even though this is approximately three times the value reported for the one test used as an example in the article. Depending on operating conditions, type of stoker and coal used the percentages of these small size particles vary from 5 to 30 per cent at Hudson Avenue.

Mr. Stern also takes issue with the statement in the article that the same apparatus and testing technique (namely the method described) is suitable for determining the amount of dust leaving stacks, the efficiency of dust separating apparatus and the fly-carbon loss on steam-generating unit-efficiency tests. The author's answer is that the method described has been used by the Brooklyn Edison Company for these three purposes since 1929 with quite satisfactory results. The United Electric Light and Power Co. has developed independently similar apparatus and procedure, a description of which can be found in a paper* by W. E. Caldwell. The New York Edison Co. has also adopted a similar method.

* "Characteristics of Large Hell Gate Direct-Fired Boiler Units," by W. E. Caldwell, ASME Trans. Feb. 1934, page 73.

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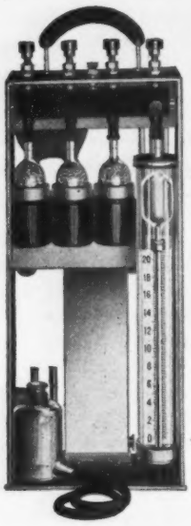

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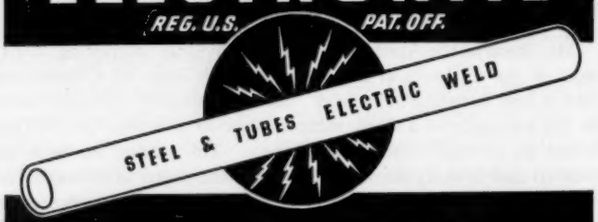

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The weld is as strong as the wall. Diameter, concentricity and wall thickness are absolutely uniform. Inside and outside surfaces are smooth and free from scabs, slivers and rolled-in scale. Tubes are full-normalize-annealed, soft, ductile and of uniform grain structure. Every tube is tested at pressures far in excess of code requirements.
Because of these features, Electrunite Boiler Tubes make possible tighter joints with worth while savings in time and labor, and add to the safety and life of equipment. Made in a full range of sizes for fire-tube or water-tube boilers. Write for literature.

STEEL AND TUBES, INC.
WORLD'S LARGEST PRODUCER OF ELECTRICALLY WELDED TUBING
CLEVELAND • • • OHIO
SUBSIDIARY OF REPUBLIC STEEL CORPORATION

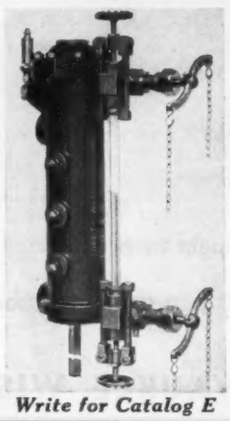
CHRONILLOY ELEMENTS

HOW MUCH IS IT COSTING you to maintain the SOOT CLEANER ELEMENTS in the HIGH TEMPERATURE positions of your boilers? Here is an element sold with an 18 MONTHS SPECIAL UNQUALIFIED SERVICE GUARANTEE. COST MORE? Yes, but WHAT SERVICE LIFE!

BALANCED VALVE-IN-HEAD

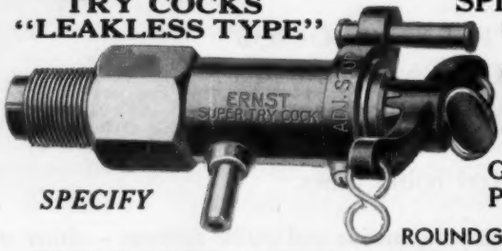
FIRST QUALITY IN DESIGN, WORKMANSHIP AND MATERIAL. Back of this IMPROVED SOOT CLEANER HEAD lies years of study to make it trouble free and give dependable service day after day. Analyze before you buy as cheap imitations may be offered.

THE BAYER COMPANY
4067 Park Ave. **St. Louis, U. S. A.**



Write for Catalog E

TRY COCKS "LEAKLESS TYPE"



SPECIFY

SPLIT-GLAND GAGES HAVE

NO

GAGE GLASS PACKING NUTS

ROUND GLASSES FOR 1000 LBS.

CAN BE ATTACHED TO ANY WATER COLUMN OR BOILER
ALIGNMENT AND STIFFENER ROD
NO GAGE GLASS PACKING NUTS
GLASS CAN BE SET AT ANY ANGLE OR VERTICAL

ERNST "SPLIT-GLAND"

ADJUSTABLE WATER GAGES, VERTICAL or INCLINED
COLUMNS & TRY COCKS FOR PRESSURES UP TO 2000 LBS.

ERNST WATER COLUMN & GAGE CO., Newark, N.J.

Agents in principal cities

NEW CATALOGS AND BULLETINS

Any of these publications will be sent on request.

Automatic Pulverizers

Raymond Bros. Impact Pulverizer Company (a division of Combustion Engineering Company, Inc.) has issued an attractive 32-page bulletin describing its impact type of mills for grinding soft and medium hard materials. These units include the "Imp" pulverizers with swing-hammer construction, the automatic pulverizers with either fixed blades or swing hammers, and the hammer-type screen pulverizers. The "Imp" and the automatic pulverizers are equipped with air separation for classifying the product, and may also be provided with air drying systems and operated as kiln mills for drying and grinding in a single simultaneous process. Special types of kiln mills with flash drying are included. The automatic pulverizers, equipped with air separation, are especially suited for plants having comparatively small grinding requirements. Typical applications of these machines are given and their performance discussed.

Automatic Self-Priming Monobloc Centrifugal Pump

A pump that will prime itself when necessary for use in sumps, cellars, isolated water supply, and numerous industrial plant services has been brought out by Worthington Pump and Machinery Corporation and is described in a bulletin just off the press. The self priming feature is attained by placing a "Hytor" on the same shaft with the motor and pump. The only requirement is a reasonably tight suction line. When the pump is primed, a pressure-operated cutout automatically unloads the "Hytor." There is no recirculation of water and no floats. The pump is available for single or polyphase 50 or 60-cycle alternating current as well as for direct current operation.

Beco-Turner Baffles

The Plibrico Jointless Firebrick Company, which has acquired the Beco-Turner baffle walls from the former builders, the Boiler Engineering Company, has issued a bulletin showing by means of photographs and blue prints, the application of these baffles to various types of water-tube boilers.

Combustion Indicators

Bulletin 341 issued by the Ess Instrument Company describes a line of combustion indicators which employ the photo-electric cell, or "electric eye" to indicate the density of haze or smoke in the products of combustion. The indicators are of several kinds involving light signals to give warning when combustion is out of bounds, a horn to give audible indication or a recorder to show the time and duration of smoke.

Condenser Tubes

A booklet being distributed by the Scovill Manufacturing Company describes installation methods and ferrule specifications for condenser tubes made by that company. It also contains data on the four Scovill condenser tubing alloys and includes net price lists for tools used for installing tubes.

Draft, Pressure and Differential Recorders

The Hays Corporation in its Bulletin No. 2017 describes a new line of draft, pressure and differential recorders for ranges between 0.1 in. and 100 in. of water, total scale. Series "OT" are applicable to the higher ranges and series "OH" to the low ranges of differential pressure. Seth Thomas spring-driven clocks are standard with both types but Telechron electric movements can be substituted if desired. The bulletin describes the construction of these recorders and their application.

Horizontal Return-Tubular Boilers

An eight-page catalog covers general specifications for a line of horizontal return-tubular boilers built by Combustion Engineering Company, Inc., New York. These boilers formerly known to the trade under the names of Casey-Hedges and Walsh-Weidner have a reputation of many years standing. Both riveted and fusion, welded construction for the shells is shown and various details of the boilers, grates, breechings, etc. are included, as well as general information on settings.

Induced-Draft Cooling Tower

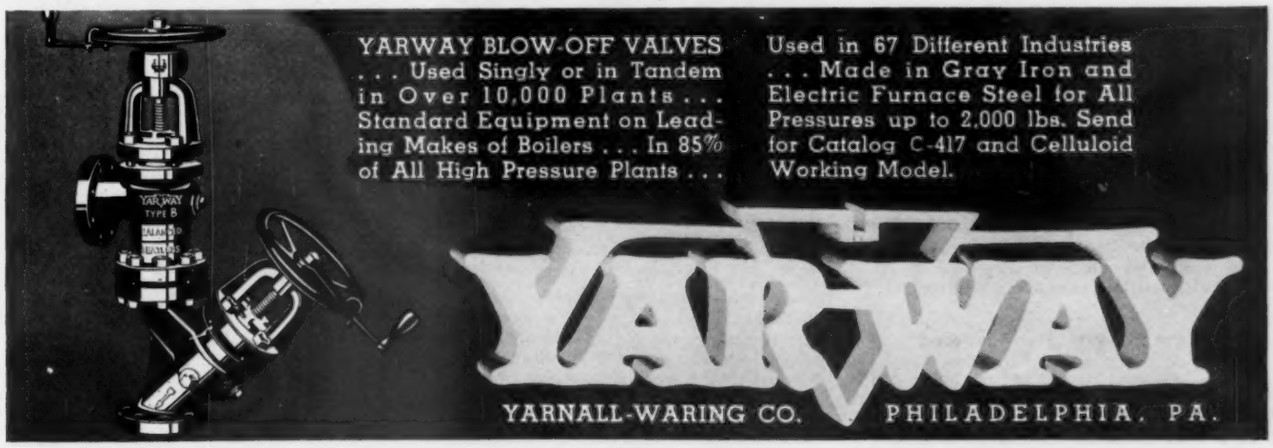
A descriptive bulletin is now available giving engineering, installation and operating data on a new line of induced-draft cooling towers, with a cooling capacity from 5 to 200 gpm, as manufactured by the Binks Manufacturing Company. The water distribution in these towers is secured through the use of Binks low-pressure clog-proof "Rotojet" nozzles which spray a finely atomized mist of water downward through upward currents induced by the fan at the top of the tower. Depending upon the size of the towers one or more fans are used. The towers are of heavy steel framing surrounded by a sectional copper-bearing galvanized steel housing asphalted and aluminum painted inside and out.

Meters for Steam, Liquids and Gas

A 48-page bulletin, No. 200, covering its complete line of meters for industrial use with steam liquids and gas has just been issued by The Foxboro Company. Of particular interest is the description of the new universal flow meter which has been developed to measure any of these fluids or gas. In addition to the sections describing flow meters at work, and the types of meters and their functions, there is a section covering very completely the construction details. Much information on flow of fluids and their measurement is included.

Oxy-Acetylene Welding

Linde Air Products Company is distributing two booklets dealing with oxy-acetylene welding. One, entitled "Precautions and Safe Practice" discusses welding and cutting, and the other, entitled "Recommended Practices for Gas Cutting of Structural Steel" discusses the qualifications for good workmanship.

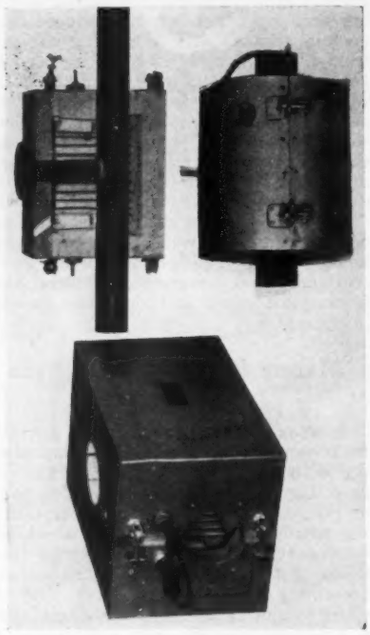

YARWAY BLOW-OFF VALVES . . . Used Singly or in Tandem in Over 10,000 Plants . . . Standard Equipment on Leading Makes of Boilers . . . In 85% of All High Pressure Plants . . .
Used in 67 Different Industries . . . Made in Gray Iron and Electric Furnace Steel for All Pressures up to 2,000 lbs. Send for Catalog C-417 and Celluloid Working Model.
YARWAY
YARNALL-WARING CO. PHILADELPHIA, PA.

NEW EQUIPMENT

of interest to steam plant engineers

Heaters for Stress Relieving Welded Piping

To relieve local stresses set up during welding operations on piping and fittings, H. O. Swoboda Inc. of Pittsburgh has brought out two designs of "Falcon" electric heaters for stress relieving in the field. One is of cylindrical form for application to welded seams in high-pressure piping and



the other is of rectangular form adapted to stress relieving nozzle welds.

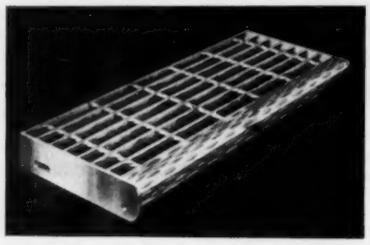
The heater is in two sections, hinged in the first mentioned type and clamped together in the second. It consists of nickel-chromium heating elements, refractory plates backed by insulation and a steel casing having high-temperature insulating board ends. A thermocouple opening is provided in the side of the heater for reading the temperature of the pipe.

One size of unit can be used for several pipe sizes. That is a heater designed for 4-in. pipe can be used for 3-, 2- and $1^1/_2$-in. pipe by inserting refractory bushings. Also the end insulation is removable so that the heater can be used for stress relieving the welds of pipe bends. The heating area of the units is such that the weld and a certain distance on each side can be slowly raised to a temperature of 1200 F.

The cylindrical hinged-type heaters are supplied for pipes up to 8 in. diameter, and for larger pipes they are built in three or more segments which are strapped around the pipe. They are designed for standard operation with 110, 220 and 440 volts and can be furnished for operation with welding machine generators.

New Heavy Stair Tread

This new stair tread has been developed by Blaw-Knox Company, Pittsburgh, to provide extreme strength against impact. It is now manufactured using a nosing made from rolled diamond checkered plate. This nosing is made to withstand abuse, particularly that given to treads when buildings are under construction.

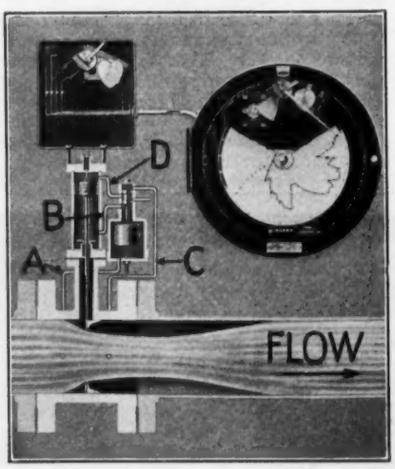


It defines the edge of each tread because of the very definite contrast between the checkered plate and the grating construction. The intersections of the bars are electroforged into one piece under enormous pressure. This is done without cutting, slotting or punching the bars or the removal of metal in any way. It thus eliminates loose parts and any tendency to rattle. The twisted cross-bar feature of the grating affords a grip for shoe soles and thus practically eliminates the danger of slipping even if the tread is wet, greasy or icy.

Flow Meter Using Varying Orifice

A new type of flow meter, which utilizes a varying orifice, is now being manufactured by the Elgin Softener Corporation of Elgin, Ill. As the flow of steam, water, oil or other liquid or gas varies, the orifice opens and closes.

In the past the measurement of flow through a pipe has usually been based on measuring the variation in the pressure drop across a fixed orifice in the line. In the Elgin Isometer a constant pressure

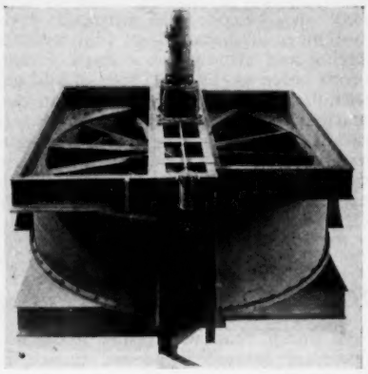


drop is maintained by changing the orifice opening. The flow is then accurately determined by measuring the amount of orifice opening at any instant. It is claimed that the varying orifice principle of operation makes it possible to measure low rates of flow accurately down to as low as $2^1/_2$ per cent of the meter capacity. It is also said that pulsating flows can be more accurately measured. Errors due to friction are also said to be eliminated because the power of the actuator is far in excess of that actually required to move the orifice gate and the metering units are electrically driven.

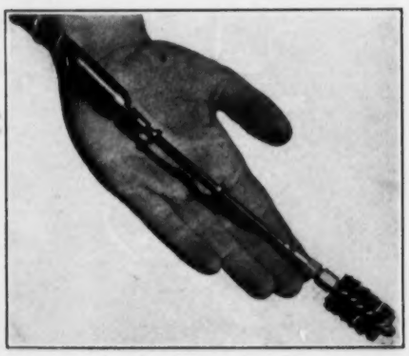
The movement of the orifice gate and the changing of that movement into an electrical impulse, that can be registered by remotely located indicating, recording or totalizing electrical meters, has been worked out in an ingenious way.

Ljungstrom Air Preheater with Center Support and Drive

The Air Preheater Corporation, 60 East 42nd St., New York, has developed a center support and drive for the Ljungstrom air preheater. This construction does away with carrying rolls, rack and track, and thus materially reduces the number of working parts, at the same time affording a simpler method of supporting



the rotor and driving motor. A large center post is employed, which is supported by a thrust bearing at one end and has a guide bearing at the other end. By this method of a single center support it is possible to adjust the rotor with less clearance between it and the rubbing surface; hence more effective sealing against leakage is provided.

Cleaner for Small Diameter Tubes

A new cleaner, designed especially for small diameter tubes of condensers, heat exchangers, etc., has just been announced by the Roto Company of Newark, N. J. This cleaner, which is air driven and which is designated as "Roto Junior," uses the well known "Rotocentric" principle, as employed in the larger machines and operates at pressures from 30 to 75 lb with an air consumption of 12 to 20 cu ft of free air per min.